• Volume 9A, Number 3—4, November 1960

BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL

Section A

CHEMISTRY

Bull. Res. Counc. of Israel. A. Chem.

Page

161 The thermal hydrolysis of metal chlorides, II. Cobaltous chloride and manganous chloride — *A. Glasner and I. Mayer*

173 The influence of some volatile elements on the intensities of spectral lines of Sm, Eu, Gd and Dy in the DC arc — *Sima Held*

177 Equilibrium studies in the system KCL-HCL-nBuOH-H_2O. — *R. Blumberg, P. Lewi and P. Melzer*

185 Metal ketyls as initiators of polymerisation of vinyl monomers. Polymerisation of acrylonitrile, styrene and methyl methacrylate by disodium benzophenone — *A. Zilkha, P. Meta and M. Frankel*

193 Organic fluorine compounds, Part XVIII. The reaction of diethyl oxalofluoroacetate with aromatic hydrocarbons — *I. Shahak and E.D. Bergman*

195 Specific ionic effects on reaction rates: The reaction between bromoacetate and hydroxyl ions — *Miryam Bobtelsky, B. Perlmutter-Hayman and G. Stein*

200 An approximate treatment of the kinetics of reversible parallel reactions — *Assa Lifshitz and B. Perlmutter-Hayman*

204 The synthesis of dl- and d-podocarpan-6-one, potential intermediates for the synthesis of diterpenes — *F. Sondheimer and M. Gibson*

LETTERS TO THE EDITOR

206 The thermal decomposition of ammonium perchlorate in the presence of magnesium oxide — *A. Hermoni (Makovky) and A. Salmon*

207 The pulse technique in the isotope separation by electromigration — *Michael M. Benarie*

BOOK REVIEWS

PROCEEDINGS

215 Of the XXVIIth meeting of the Israel Chemical Society

INDEX TO VOLUME 9A

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THE THERMAL HYDROLYSIS OF METAL CHLORIDES

II. COBALTOUS CHLORIDE AND MANGANOUS CHLORIDE

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ABSTRACT

The thermal hydrolysis of anhydrous cobaltous chloride and manganous chloride, in the temperature range 400 – 500°C, proceeds, after a short induction period, at a linear rate up to 80 – 85 % of the chlorine content of the samples. In both cases the solid product is the simple oxide MO.

The various factors, such as weight of samples, exposed surface, rate of flow of inert gas and water vapour pressure, affect the rate of hydrolysis in a similar way to that observed with anhydrous nickel chloride[1].

The sequence of reactions is composed of 1) adsorption of water on the exposed surface of the salt and intrusion of water molecules between the lattice layers in proportion with the increasing vapour pressure, 2) detachment of hydrogen chloride and formation of an intermediate hydroxy-chloride (rate-determining), 3) decomposition of the hydroxide into an oxide. The activation energies are in inverse order of the radii of the cations.

It is suggested that in the case of hydrated chlorides containing the chloride ions in their inner sphere, e.g. $[CoCl_2(H_2O)_4]2H_2O$, dehydration precedes hydrolysis, whilst in the case of chlorides with chloride ions in the outer ionic sphere, e.g. $[Mg(H_2O)_6]Cl_2$, hydrolysis and dehydration of the last water molecules proceed simultaneously.

INTRODUCTION

The study of the thermal hydrolysis of metal chlorides has been continued, using the same methods of investigation as in the previous work on cupric chloride and nickel chloride[1]. The lattice structures of the anhydrous salts treated in this articles are very similar to the hexacoordinated layer structure[2] of anhydrous nickel chloride, and so also are the mechanisms of the hydrolytic reactions indicated by the experimental results obtained. The quantitative differences are explained by differences in the lattice constants and the specific nature of the respective cations.

The structure of the hydrated salts has also been investigated by various authors. In the case of cobalt, the two chloride ions and four water molecules are said to be octahedrally coordinated, while the other two water molecules are relatively free[3].

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* This article is part of a Ph. D. thesis submitted to the Senate of The Hebrew University of Jerusalem

Received March 8, 1960

The cell dimensions of the tetrahydrated manganous chloride are larger in two directions than those of the cobaltous chloride hexahydrate[4]. Both salts are monoclinic.

	a	b	c		β
$CoCl_2.16H_2O$	10.34	7.06	6.67	A°	122°19′
$MnCl_2.4H_2O$	11.90	9.55	6.15	A°	111°

EXPERIMENTAL

The materials used were cobaltous chloride hexahydrate $CoCl_2.6H_2O$, and manganous chloride tetrahydrate $MnCl_2.4H_2O$, "Baker Analyzed" reagents. Stocks of the anhydrous salts were prepared by heating them in a current of hydrogen chloride gas [5] at 180–200°C; they were kept in a desiccator over phosphorus pentoxide. Even so, the cobaltous chloride absorbed moisture, and some of the experiments were made with samples containing up to 8% water, as indicated by analytical determinations of the cobalt.

The samples were weighed in a platinum (or porcelain) boat, and heated in a horizontal oven. A regulated current of nitrogen, saturated with water vapour at a known pressure, was passed over the heated samples, and carried with it the hydrogen chloride gas formed in the hydrolysis. The latter was absorbed in a conductivity cell containing distilled water. By frequent measurements of the conductivity of this solution, the rate of hydrolysis was closely followed and recorded[1].

RESULTS

1. *Cobaltous Chloride*

Runs were made between 430° to 500°C. The general appearance of the conductivity *versus* time curves obtained is of the S type for both the anhydrous and the hydrous salt, as illustrated in Figure 1. Most of the experiments recorded here were made with the anhydrous salt. After a very short period of induction, the increase of conductivity is linear up to 80% of the chlorine content of the sample. The slopes of the linear part of the curves were designated by k, and a number of factors, found to affect the rate of hydrolysis, were studied and compared by means of this constant.

(*a*) *Spread and weight of samples*

In Table I the k–values obtained using a porcelain boat (65 mm long) are compared with those obtained when using a platinum boat (15 mm long). In both cases, the chloride was spread to cover the whole length of the boat. The weight of the samples was also varied.

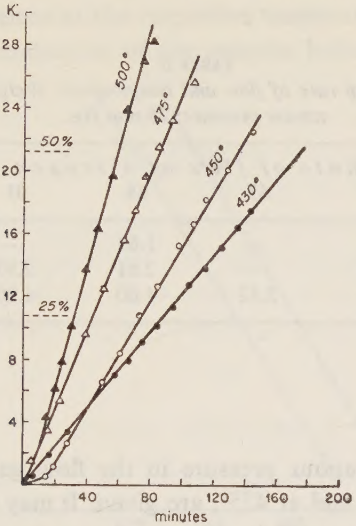

Figure 1
Conductometric measurements of the hydrolysis of cobaltous chloride at the temperatures indicated. Wt. of samples ~38 mg, flow rate (inert gas saturated with water vapour at 26.5°C) 34 ml/min.

TABLE I

Effect of weight of samples and of exposed surface on the constants k. Rate of flow of inert gas: 34 *ml/min, water vapour pressure*: 26 *mm Hg.*

°C	*Porcelain boat* *wt. (mg)*	10*k*	*Platinum boat* *wt. (mg)*	10*k*
450	33.6	3.42	24.0	1.89
			70.2	1.87
475	38.1	3.94	38.4	2.88
			68.4	2.67
500	27.4	6.10	34.6	3.89

Clearly *k* is independent of the original weight of the samples. On the other hand, the exposed surface has a profound effect on the rate of hydrolysis, *k* in experiments with porcelain boats being larger by a factor of 1.6 on the average than in those with the platinum boats.

(*b*) *Rate of flow of nitrogen*

Values of *k* obtained on varying the rate of flow of the inert gas at different temperatures are shown in Table II. On increasing the rate of flow from 34 ml/min to 68 ml/min, *k* increases at all temperatures by a factor of 1.38, but at higher rates even this small effect reduces to a minimum.

TABLE II

Values of 10*k obtained on varying rate of flow and temperature. Weight of samples*: ~38 *mg*; *water vapour pressure*: 26 *mm Hg*.

°C	*Rate of flow of nitrogen ml/min*						
	23	34	45	68	91	113	136
430	—	1.23	—	1.69	—	1.87	1.90
450	—	1.89	—	2.61	2.93	—	2.81
475	2.29	2.88	3.32	4.00	4.00	—	—

(*c*) *Water vapour pressure*

The influence of water vapour pressure in the flow gas is shown in Table III. Two series of runs, at 450° and at 475°, are given. It may be seen that rather small pressures, 0.44 mm Hg, were sufficient to produce a comparatively high rate of hydrolysis, but on increasing the vapour pressure up to 26 mm Hg, only minor, approximately linear, effects on *k* were observed.

TABLE III

Variation of 10*k with water vapour pressure. Weight of samples*: 38 ~*mg*. *Rate of flow*: 34 *ml/min*.

Water vapour pressure in mm Hg		0.44	7.8	13.8	19.0	26.0
10*k*	at 450°C	0.81	1.45	1.74	1.80	1.89
	at 475°C	1.38	1.90	2.22	2.48	2.88

(*d*) *Temperature coefficient*

The logarithms of the rate constant *k* plotted against the inverse of absolute temperature, at different rates of flow, lie on parallel straight lines (Figures 2). From the slope of these the energy of activation 17.8 kcal/mole was calculated.

(*e*) *Experiments with cobaltous chloride hexahydrate*

As already mentioned, the decomposition curves of the hydrated salt were similar to those of the anhydrous chloride, except that the time of induction was somewhat longer. In Table IV, the constants k obtained with two series of runs at various temperatures are compared. These runs were made in porcelain boats, as the sudden heating of the hydrated samples in the platinum boats caused some spitting. The agreement between the values at the respective temperatures was surprisingly good, indicating a complete dehydration of the samples before hydrolysis.

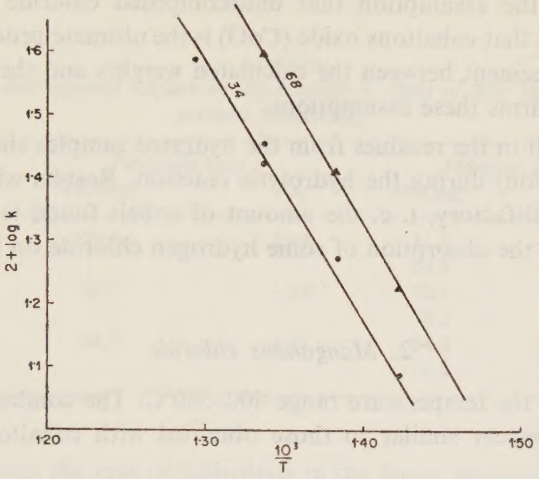

Figure 2
log k vs. $10^3/T.CoCl_2$. Numbers on curves show rate of flow in ml/min.

TABLE IV
Comparison of k with (a) hydrated and (b) anhydrous cobaltous chloride. Porcelain boats. Weight of samples: ~70 mg and ~33 mg respectively. Rate of flow; 34 ml/min. Vapour pressure: 26 mm Hg.

Temp. °*C*		430	450	475	500
10k	a	2.54	3.58	4.00	6.13
	b	2.59	3.42	3.94	6.10

(*f*) *Weights and analyses of partly hydrolysed samples* are recorded in Table V. The solid residues were weighed, dissolved in sulphuric acid, and their cobalt content determined by a spectrophotometric method with nitroso-R salt[6].

TABLE V
Analyses of partly hydrolysed samples.

Wt. of sample	*% of hydrolysis*	*Wt. of residue*		*Wt. of cobalt*	
		weighed	*calc.*	*detd.*	*calc.*
*74.9	49.6	31.8	32.3	18.6	18.6
*88.3	90.2	28.2	29.8	22.2	21.9
24.2	46.6	18.2	19.4	—	—
29.1	53.4	24.1	22.6	12.0	13.2
39.0	65.3	28.5	28.2	16.8	17.7
27.5	66.7	19.7	19.7	11.5	12.4
22.2	69.7	15.0	15.7	—	—
28.7	76.9	18.0	19.4	—	—

* The first two samples were the hydrate $CoCl_2.6H_2O$, all the rest the anhydrous salt.

Anhydrous cobalt chloride, being extremely hygroscopic, unavoidably absorbed some water vapour upon weighing. On the basis of a few analyses, this absorption was estimated at approximately 6% ($\pm$ 2) of the weight of the sample, and was deducted from the weights recorded in the Table. Making use of the percentage of hydrolysis known from the conductivity measurements, the weight of the residue was calculated on the assumption that undecomposed chloride is present in its anhydrous form and that cobaltous oxide (CoO) is the ultimate product of the hydrolysis. The good agreement between the calculated weights and the actual weights of of the residues confirms these assumptions.

Analyses of cobalt in the residues from the hydrated samples show that no cobalt is lost (by sublimation) during the hydrolytic reaction. Results with the anhydrous chloride are less satisfactory, i. e. the amount of cobalt found is consistently low. This may be due to the absorption of some hydrogen chloride on the surface of our preparations.

2. *Manganous chloride*

Runs were made in the temperature range 400–500°C. The conductivity *versus* time curves (Figure 3) appear similar to those obtained with cobaltous chloride, with either the anhydrous or the hydrated salt. After a very short period of induction, the increase of conductivity is linear up to 85% of the chlorine content of the samples.

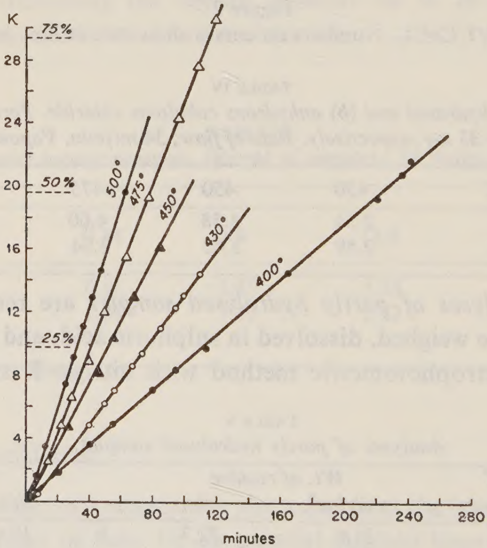

Figure 3
Conductometric measurements of the hydrolysis of manganous chloride at the temperatures indicated. Wt. of samples $\sim$34 mg, flow rate (inert gas saturated with water vapour at 26.5°C) 34 ml/min.

Most of the results given are from runs with the anhydrous chloride, unless otherwise stated.

(*a*) *Weight and spread of samples*

The influence of these factors on constant k is shown in Table VI.

TABLE VI

The effect of weight and exposed surface on the constant k. Rate of flow 34 *ml/min. Water vapour pressure* 26 *mm Hg.*

°C	Porcelain boat wt. (mg)	10k	Platinum boat wt. (mg)	10k
430	29.5	2.43	31.5	1.41
			64.8	1.71
450	36.5	3.18	30.6	1.96
			74.5	2.20
475	34.3	4.81	34.9	2.69
			61.8	3.18

It may be seen that the rate of hydrolysis in the larger porcelain boat is about 1.7 times faster than in the platinum boat. The weight of the samples has also a small effect on k, which may be expressed by a factor of 1.2 on doubling the weight of the samples. This behaviour of manganous chloride is exceptional, no such effect having been noted with any of the other chlorides investigated by us before.

(*b*) *Rate of flow of nitrogen*

The variation of k with the rate of flow, at different temperatures, is shown in Table VII. With small rates of flow (F), up to about 68 ml/min, $k = k_F\sqrt{F}$. With higher rates of flow, k remains constant (or even decreases slightly).

TABLE VII

The influence of the rate of flow of nitrogen on 10*k. Weight of samples:* ≈33 *mg. Water vapour pressure:* 26 *mm Hg.*

Temp. °C	Rate of flow of nitrgoen ml/min. 23	34	45	68	91	136
400	—	0.87	—	1.29	1.11	1.05
430	—	1.41	—	1.77	1.90	2.03
450	1.56	1.96	—	2.82	2.72	2.60
475	2.13	2.69	—	3.82	—	4.08
500	2.70	3.16	3.65	—	—	—

(*c*) *Water vapour pressure*

The influence of water vapour pressure in the flow gas may be seen in Figure 4. Two series of runs are shown, one at 450°C and the other at 475°C. In both cases, low vapour pressures cause a large increase in the constant *k*, and from a vapour pressure of about 1.5 mm Hg upwards the increase in *k* is approximately linear.

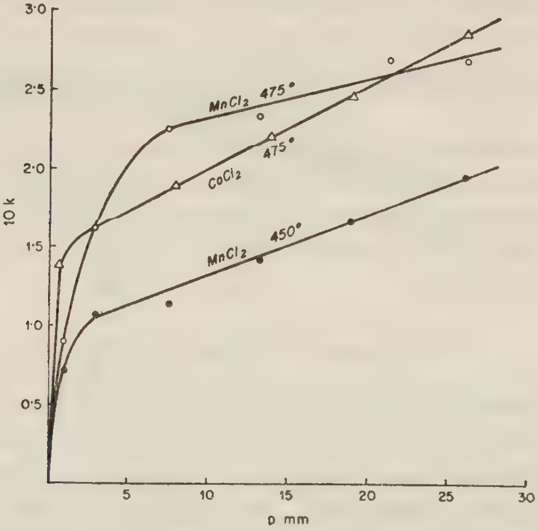

Figure 4
Influence of water vapour pressure in flow gas on rate of hydrolysis of manganous chloride at 450°C and at 475°C (corresponding results with $CoCl_2$ were also plotted for comparison).

(*d*) *Temperature coefficient*

In Figure 5 the log *k* values of three series of runs with different rates of flow of nitrogen were plotted aganist the inverse of absolute temperature. The slope of the parallel straight lines so obtained give the activation energy 14.65 kcal/mole.

(*e*) *Experiments with manganous chloride tetrahydrate*

The results with the tetrahydrate are compared in Table VIII with those of the anhydrous salt. The shapes of the hydrolysis curves were similar to those obtained with the anhydrous salt, only the periods of induction were longer, and the rate of reaction, as expressed by *k*, faster by a factor of 1.3.

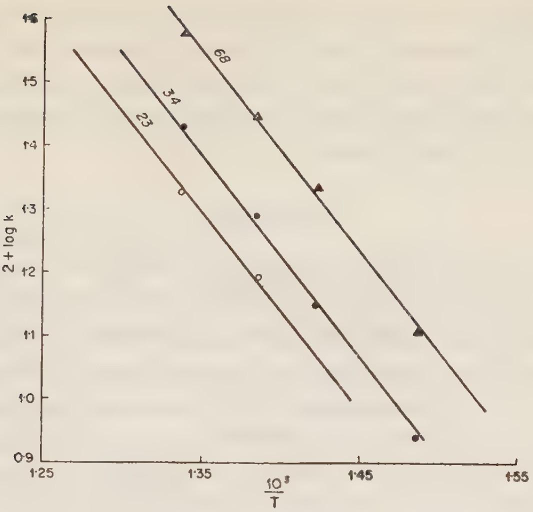

Figure 5
log k *vs.* $10^3/T$. $MnCl_2$. Numbers on curves show rate of flow in ml/min.

TABLE VIII
Constants k of manganous chloride tetrahydrate (a), compared to the anhydrous salt (b). Weight of samples: $MnCl_2$ *~34 mg,* $MnCl_2.4H_20$ *~70 mg*

Temp. °C.		430	450	475
$10k$	*a*	1.69	2.66	3.51
	b	1.41	1.96	2.69

(*f*) *Weights of partly hydrolysed samples* are recorded in Table IX. Calculations were made on the assumptions that the end product of the hydrolysis is manganous oxide MnO, and the part undecomposed is the anhydrous salt. The percent of hydrolysis is given by the conductivity measurements.

TABLE IX
Weight of partly hydrolysed samples.

Temp. °*C*	*Wt. of sample* (*mg*)	*% of hydrolysis*	*Weight of residue*	
			Weighed	*Calc.*
400	26.7	41.0	21.4	21.94
430	64.8	30.8	56.4	56.10
450	33.8	51.3	26.6	26.24
*450	72.3	42.1	35.0	37.54
475	31.7	61.6	22.4	23.17
475	34.2	68.1	24.0	24.03

* $MnCl_2.4H_2O$

There is a good agreement between the weighed and the calculated values of the residue, confirming the observation that manganous chloride does not sublime at the temperatures of the experiments, and also the assumption with respect to the oxide formed. If the tetroxide Mn_3O_4 had been produced, the weights of the residues would have been 3–6% higher than that calculated.

DISCUSSION

The general features of the hydrolysis of anhydrous cobaltous chloride and manganous chloride are similar to those of the anhydrous nickel chloride with regard to all the factors studied, and in accord with the very similar structures of these three chlorides. The reactions proceed at a conveniently measurable rate in the temperature range 400–500°C, forming the divalent oxides MO. The rate of hydrolysis is linear, after a very short period of induction, up to 80–85%, and may be expressed by the simple constant k. This is found to be independent of the weight of the samples (excepting manganous chloride, in which case k is slightly affected by a change of weight), but varying with the extent of the exposed surface. The variation of k with water vapour pressure resembles the Freundlich absorption isotherm (see Figure 4), indicating that the site of the hydrolytic reaction is on the exposed surface of the salt with adsorded water molecules. The effect of the water vapour pressure may be divided into two parts: 1) that due to the saturation of surface, and 2) the part due to the intrusion of water molecules between the lattice layers at higher pressures. In the case of the nickelous and cobaltous chlorides, a few tenths of a mm of pressure sufficed for the saturation of the surface; with manganous chloride, about 1.5 mm pressure was necessary to attain this point. Thus, in the case of manganous chloride, there is a less abrupt passage from surface adsorption to interlayer absortion, the distance between the layers being probably somewhat greater. The exceptional influence of weight in the case of manganous chloride is also probably connected with the possibility of diffusion and absorption of water molecules in deeper layers.

The rate of flow of nitrogen causes an increase of k only up to about 68 ml/min, owing to faster desorption and diffusion of the hydrogen chloride into the flow gas. The effect of higher rates of flow is negligible.

The activation energies (E) are compared in the following to the cationic radii[7] (RC) and to the heat of reaction[8] (ΔH):

$$MCl_2 + H_2O \longrightarrow MO + 2\,HCl + \Delta H \qquad (1)$$

	$MnCiCl_2$	$CoCl_2$	$NiCl_2$	
E	14.65	17.8	18.6	kcal/mole
ΔH	–35.61	–33.16	–30.3	” ”
RC	0.91	0.82	0.78	A°

Obviously, the heats of reaction are much higher than the energies of avtivation and vary in the opposite direction. Hence, the hydrolytic reaction is not that represented in equation (1). On the other hand, the activation energies may be related to the ionic radii, the first increasing with the decrease of the latter. It is therefore concluded that the scission of the bond between the metal and the chloride ion is the rate-determining step in the sequence of reactions composed of the following:

1. Adsorpion of water molecules
   $H_2O + MCl_2 \rightleftharpoons H_2O \;..\;..\;..\; MCl_2,$
2. Activation of the chloride ions and formation of hydroxy-chlorides
   $H_2O \;..\;..\;..\; MCl_2 \longrightarrow M(OH)Cl + HCl,$
3. Dehydration and formation of the oxide
   $2\,M(OH)Cl \longrightarrow MO + MCl_2 + H_2O,$

because of the instability of the hydroxy-chlorides at these temperatures.

In contrast to the anhydrous salts, the behaviour of the hydrated chloride is different in each case. Cobaltous hexahydrate is hydrolysed at the same rate as the anhydrous salt. In fact, it is completely dehydrated during the period of induction, in this respect resembling cupric chloride dihydrate. Manganous chloride also undergoes dehydration befoer hydrolysis (see Table VIII), yet the rate of hydrolysis of the hydrated samples is faster than that of previously dehydrated samples. This difference may be attributed to a more open structure of the freshly formed anhydrous salt, i. e. it "remembers" its previous structure, so that water molecules diffuse between the lattice layers at a lower vapour pressure.

Of the four chlorides studied, only nickelous chloride hexahydrate reacts to an appreciable extent with its own water of crystallization, resembling magnesium chloride in this respect. Hence it is suggested that this behaviour is characteristic for the hydrated salts that do not contain chloride ions in the coordination sphere of the cation. Cupric chloride[9] and cobaltous chloride[3] are known to have both chloride ions directly bound to the metallic ion. Manganous chloride tetrahydrate[4] has a similar structure to cobaltous chloride hexahydrate, suggesting that manganese is sexacoordinated by four water molecules and two chloride ions. The two more distant water molecules found in the cobaltous salt are missing in the manganous salt. Therefore, when heated, the three chlorides mentioned are at first dehydrated, and only later hydrolysed by reacting with absorbed water vapour.

Nickelous chloride hexahydrate is also said to have a similar structure to its cobaltous analogue[3], yet from the present results it would appear that it has six water molecules in its inner shpere, and two chloride ions outside the coordination sphere, perhaps in positions occupied by the two distant water molecules in the cobaltous salt. This conclusion is strongly supported by the known tendency of the discussed cations to form, or not to form, chloro-complexes in solution[10].

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THE INFLUENCE OF SOME VOLATILE ELEMENTS ON THE INTENSITIES OF SPECTRAL LINES OF Sm, Eu, Gd AND Dy IN THE DC ARC

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ABSTRACT

An extremely strong temperature dependence of the intensity ratio of atom and ion lines of Eu was observed. The shape of the lines of Sm, Eu, Gd and Dy changes in the presence of elements with different ionisation potentials. Using Li_2CO_3 as a "carrier", a satisfactory sensitivity for Sm, Eu, Gd and Dy in graphite powder may be obtained in the DC arc.

Some observations were made in connection with the determination of Sm, Eu, Gd and Dy in U_3O_8 [1]. The rare earths and other impurities were removed from uranium by ion exchange using a Dowex-1-hydrochloric acid system as described by Brody, Faris and Buchanan[2]. In spite of the satisfactory results obtained by a spectrographic analysis of the concentrated effluent solution using the copper spark method[3] some experiments were made in order to obtain a satisfactory sensitivity also using a DC arc. This may be important in the case, where the presence of many other impurities in large quantities in the solution does not permit the use of the copper spark method.

In order to check the conditions giving the best sensitivity for the elements to be determined, 1 ml of standard solution containing 1 μg/ml of Sm, Eu, Gd and Dy was evaporated to dryness with 20 mg of pure graphite powder plus 5 mg of various compounds of some volatile elements. The sensitivity obtained without addition of a "carrier" to the graphite powder was very poor. Table I shows the compounds used and the ionisation potentials of the respective elements under examination.

TABLE I
The compounds used and the ionisation potentials of respective elements under examination

Element	*Compound used*	*I.P. of the respective elements under examination (V)*
K	K_2CO_3	4.32
Li	Li_2CO_3	5.36
Ga	Ga_2O_3	5.97
Ge	GeO_2	8.09
Zn	ZnO	9.36

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Working conditions are given in Table II.

TABLE II
Working conditions

Spectrograph	Hilger Automatic, No E 478, Glass optics	
Wavelength range	3860—5500A	
Analysis lines (A)		**EuI 4627.12**
	SmI 4296.75	EuI 4594.02
	SmI 4336.13	EuI 4661.87
	SmII 4334.16	EuII 3907.11
	SmII 4280.80	EuII 3930.50
	SmII 4256.4	EuII 3971.99
	GdI 4346.46	EuII 4129.74
	GdII 4313.85	
	DyII 4000.45	
	DyI 4211.72	
Mode of illumination	The image of the light source was projected onto the slit	
Slit width	0.015 mm	
Light source	DC arc, 10 amp	
Electrode gap	6 mm	
Electrodes	UCP spectro-tech. graphite. Upper electrode of 4.5 mm diameter with rounded end. Lower electrode of 6 mm diameter, 3 mm deep, a wall thickness of 0.7 mm	
Samples	20 mg graphite powder + $1\mu g$ of Sm, Eu, Gd and Dy + 5 mg of one of the compounds shown in Table I	
Exposure time	Burned till the "carrier" was present. With K_2CO_3 — 35 sec., Li_2CO_3 — 50 sec., Ga_2O_3 — 15 sec., ZnO — 10 sec.	
Photographic plates	Eastman Spectrum Analysis No 2 or 103F	
Developing	D–19, SA2 — 5 min., 103F — 3 min., 20°C	

Most characteristic is the behaviour of the Eu atom and ion lines. The lines of EuI are very much enhanced in the presence of the elements with low ionisation potentials and almost not visible with the elements of high ionisation potentials. On the other hand the intensity of the EuII lines is hardly affected by the presence of elements of different ionisation potentials. Because the behaviour of the Eu 3971.99 A line is similar to the behaviour of the EuII 3907.11 A and EuII 3930.50 A lines it was supposed, that the line Eu 3971.99 A must be also classified as EuII line and not as an atom line as suggested by Harrison[4] and Gatterer[5] This is in accordance with the data of King[6] and Russel, Alberston and Davis[7].

Fig. 1 shows how the intensity ratio of EuI and EuII lines is affected by the presence of "carrier" elements with different ionisation potentials. Such an extremely strong dependence on temperature of the intensity ratio of a pair of lines has been observed by several authors in the case of Ca and Sr [8,9]. Analogous intensity changes for atom and ion lines of Eu and alkaline earth elements are probably caused by analogous structures of the external shell of electrons.

Furthermore it was observed that the ion lines of Sm, Eu, Gd and Dy are most

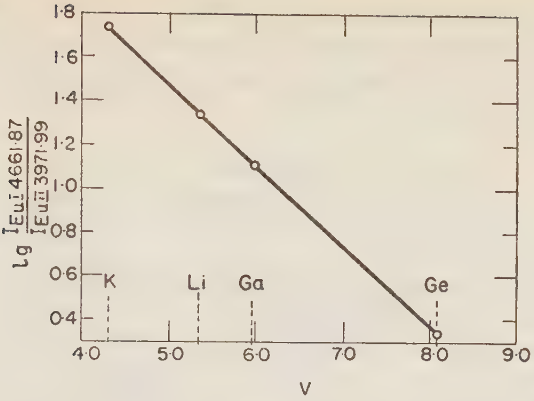

Figure 1
The dependence of intensity ratio of atom and ion lines of Eu on the ionisation potential of the element added

intense in the presence of Li_2CO_3 and Ga_2O_3. Probably the temperature of the arc in the presence of Li or Ga is optimal for the excitation of the ion lines because of the relatively low excitation potential of the singly ionized atoms of the rare earth elements.

In order to check other possible causes of this enhancement the longitudinal distribution of the intensity of the spectral lines of Sm, Eu, Gd and Dy in the DC arc was investigated. Some conclusions about the longitudinal distribution of the atoms and ions present in traces could be drawn from the observed change of intensity of a line when the exposure is made with the image of the light source on the whole length of the slit. Ahrens[9] investigated longitudinal intensity variatons using such a "pole to pole" analysis. In the present work the same technique was used and it was observed that the ion lines of Eu are most intense near the cathode in the presence of K and near the anode in the presence of Zn. In the presence of Li and Ga these lines are of almost the same intensity from end to end of the electrode gap. The ion lines of Sm, Gd and Dy behave similarly. It seems to be possible that such intensity variations are an additional cause of the enhancement of the ion lines of the investigated rare earth elements in the presence of Li and Ga.

These observations on the longitudinal intensity distribution are in fair agreement with the statement by Vainstein and Belyaev[10], that the "carrier" affects the distribution of the elements in the analytical gap of the source.

Taking into account that in the presence of Li the background is weaker and the analysis lines GdI 4346.46 A* and DyII 4000.45 A are stronger, Li_2CO_3 was chosen as a "carrier" for the determination of Sm, Eu, Gd and Dy in graphite powder which was saturated with the effluent after separation from U_3O_8. The sensitivity obtained in the work reported here is compared with that of Carter and Dean[11] who also used DC arc excitation.

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* The behaviour of the GdI 4346.46 A line is different from the atom lines of Eu, Sm and Dy. This line is stronger in presence of Li. The line GdI 4225.86 A could not be investigated because of the coincidence with the strong CaI 4226.73 A line.

TABLE III
Detection limits

	Present work		*Carter and Dean* (11)	
Element	*Analysis line* (*A*)	*µg rare earth on the electrode in 20 mg graphite + 5mg* Li_2CO_3	*Analysis line* (*A*)	*µg rare earth on the electrode in a 2 to 1 graphite and ytrium rare earth mix.*
Sm	I 4296.75	0.1	4334.14	0.5
Eu	I 4627.12	< 0.1	2925.03	0.5
Gd	I 4346.46	0.1	3422.47	0.5
Dy	II 4000.45	0.2	3169.98 3407.80	0.5

This work was carried out in the Spectroscopy Laboratory of the Weizmann Institute of Science, Rehovoth. The separation of the rare earths from U_3O_8 was carried out by K. Rosenberg in the Israel Atomic Commission Laboratories.

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EQUILIBRIUM STUDIES IN THE SYSTEM $KCl-HCl-n\mathrm{BuOH}-H_2O$*

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ABSTRACT

The equilibrium system $KCl–HCl–n\mathrm{BuOH}–H_2O$ has been examined at 30°C, in those regions where two liquid phases coexist. The individual distributions of KCl, HCl and H_2O between the two phases and the dependent interrelationships were determined over a wide range of concentrations, straight line relations being found to obtain in many cases.

The equilibrium data show that the presence of KCl in the system favours the transfer of HCl to the alcoholic phase; this effect is particularly marked at lower concentrations of HCl in the aqueous phase; at high concentrations of HCl, the effect of KCl disappears.

At a given concentration of HCl in the aqueous phase, less H_2O will be present in the solvent phase at equilibrium, the higher the KCl concentration of the system.

At constant KCl concentration, the higher the HCl content of the system, the higher the H_2O concentration in the alcoholic phase.

For KCl concentrations of approximately 5% or higher in the water phase, there is a definite relationship between the amounts of HCl and H_2O present in the solvent phase at equilibrium. This relationship was found to be 5 mol H_2O for 1 mol HCl.

The system has been presented in a more generalised form by plotting the mol ratio of HCl/H_2O in the solvent versus the weight ratio of HCl/H_2O in the aqueous phase, for various levels of HCl in the aqueous phase. This gives a series of straight lines which can readily be used for interpolation purposes.

INTRODUCTION

As part of a general programme of work on the preparation of inorganic compounds by solvent extraction, the system $KCl–HCl–n\mathrm{BuOH}–H_2O$ was investigated at 30°C. To simplify graphical presentation of the multicomponent system in two dimensions, the experimental design was based on selected compositions in the aqueous phase. This made it possible to correlate the equilibrium data in a number of ways to show up dependent interrelations, while restricting all graphical presentations to planar diagrams.

In many cases the graphs indicated straight line relationships between pairs of variables. Calculation of correlation coefficients confirmed this in every case with a confidence of 99.9% or better. Equations of regression lines were calculated[1] and the best straight lines drawn through the experimental points.

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EXPERIMENTAL

Aqueous solutions of HCl in water of known concentrations were prepared, and various known amounts of KCl added. Composition of solutions were selected in such a way that results could be expressed in terms of a constant level of HCl or of KCl, as desired. An aliquot of a particular solution was introduced into a glass-stoppered measuring cylinder and *n*BuOH added; the quantity of alcohol added being small compared to the aqueous solution. The cylinder was introduced into a thermostatic bath, and when both layers had reached the temperature of the bath (30°C), the cylinder was shaken vigorously and returned to the thermostat again, until two clear layers separated. Samples of both layers were then withdrawn for analysis. The determinations generally made were: the H^+ concentrations, volumetrically, and the Cl^- by the Mohr method; the K^+ concentration was calculated, but occasionally it was determined flame-photometrically, in order to check the accuracy of the calculations. Besides, the H_2O concentration in the solvent phase was determined by the Karl Fischer method (accuracy of determination ±1–2 % relative).

RESULTS

Distribution data are recorded in Table I, while various correlations in the system are presented in graphical form (Figures 1–7). Rectangular coordinates, semi-log and log-log coordinates have been used in these correlations so as to obtain straight line relationships as far as possible. Since the water layer was not fully analysed, conventional correlations have not been applied here[2,3]. Instead, the system has been presented from the point of view of the distribution of each component between

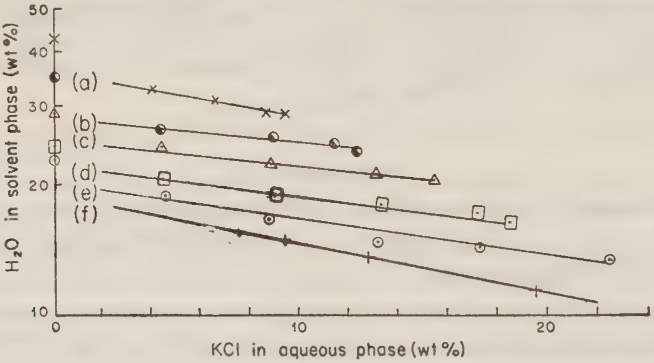

Figure 1

Line	Equation	HCl in aq. phase wt%
a	$\lg y = 1.553 - 0.00992x$	10.3 – 10.5
b	$\lg y = 1.449 - 0.0059\,x$	8.15 – 8.55
c	$\lg y = 1.3999 - 0.006\,x$	6.0 – 6.43
d	$\lg y = 1.345 - 0.0075\,x$	3.95 – 4.44
e	$\lg y = 1.3031 - 0.0083\,x$	1.94 – 2.3
f	$\lg y = 1.2745 - 0.0111\,x$	0

the two liquid phases, paying particular attention to reciprocal influences of the components with respect to distribution.

Figures 1 and 2 show the water content of the alcoholic layer as a function of the KCl and the HCl concentration in the aqueous layer, respectively. At a given concentration of hydrochloric acid in the aqueous solution, the water content of the butanol layer is smaller the higher the salt (KCl) content of the aqueous phase. The addition of a small amount of KCl to a system containing HCl–H_2O–BuOH causes a marked decrease in the water content of the organic layer; the effect of further additions of salt is less pronounced. When the system contains no HCl, (line f, Figure 1) the influence of increasing KCl content on water distribution is much more accentuated over the whole range of KCl concentration. (High concentrations of KCl cannot be attained in high concentrations of HCl). The higher the HCl concentration in the aqueous layer, the higher the concentration of H_2O in the alcoholic layer, for a particular KCl concentration. Initially, however, at lower KCl concentrations and up to ~ 4% acid (Figure 2) the influence of the acid is very small, being expressed by a nearly horizontal line at zero concentration of KCl; from this point on, i.e. for concentrations above 4% acid, the slope of the line becomes very steep. This "critical concentration" (4%) coincides with the point of intersection of the lines correlating the tie lines in the ternary system HCl–H_2O–nBuOH according to the correlation method of Treybal *et al*[4]. On increasing the KCl concentration, the effect of this change of HCl concentration is

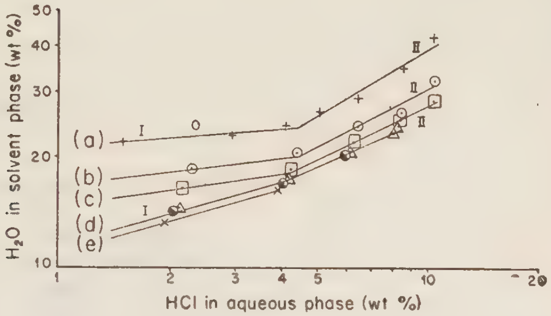

Figure 2

Line	Equation	KCl in aq. phase wt %	
a_I	$\lg y = 1.3258 + 0.086 \lg x$	0	
a_{II}	$\lg y = 0.986 + 0.6165 \lg x$		
b_{II}	$\lg y = 0.9566 + 0.54 \lg x$	4.1 - 4.66	
c_{II}	$\lg y = 0.949 + 0.507 \lg x$	8.76 - 9.06	
d_I	$\lg y = 1.064 + 0.291 \lg x$	11.5 - 13.3	△
d_{II}	$\lg y = 0.9628 + 0.45 \lg x$	15.5 - 17.3	◐
e		18.5 - 22.5	

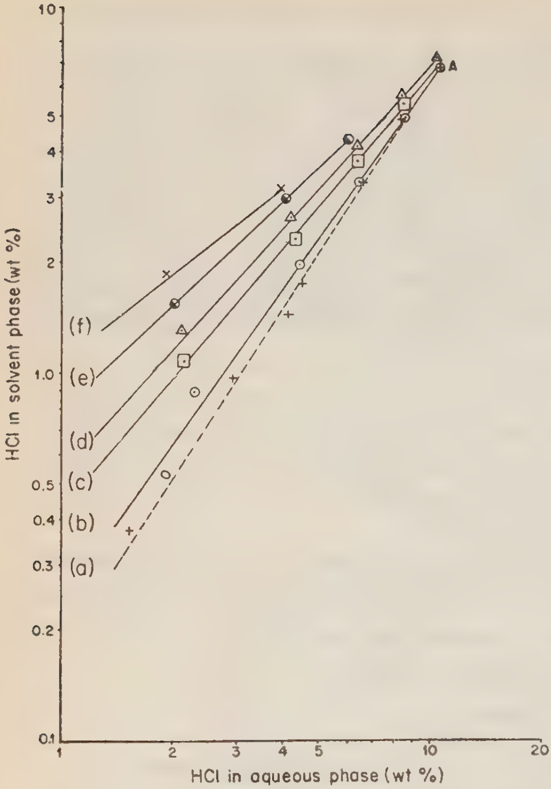

Figure 3

Line	Equation	KCl in aq. phase wt %
a		0
b	$\lg y = -0.6239 + 1.432 \lg x$	4.1 – 4.66
c	$\lg y = -0.3646 + 1.186 \lg x$	6.72 – 9.06
d	$\lg y = -0.2804 + 1.145 \lg x$	9.55 – 13.3
e	$\lg y = -0.0942 + 0.9517 \lg x$	15.5 – 17.3
f	$\lg y = 0.034 + 0.77 \lg x$	18.5 – 22.5

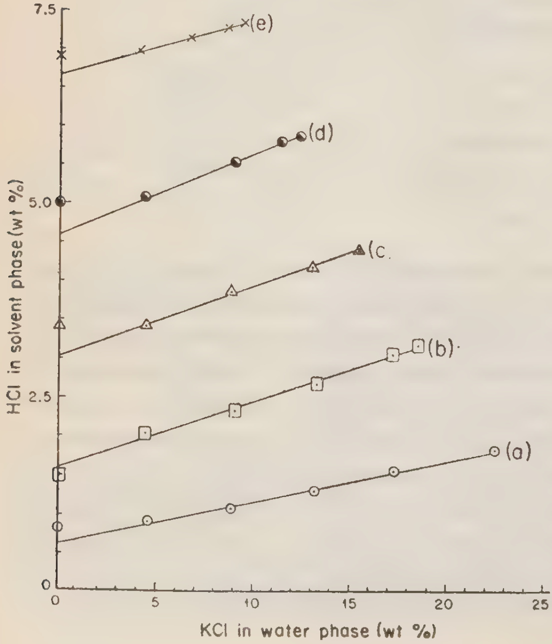

Figure 4

Line	Equation	HCl in aq. phase wt %
a	$y = 0.616 + 0.0554x$	1.94 – 2.3
b	$y = 1.607 + 0.0845x$	3.95 – 4.44
c	$y = 3.016 + 0.0904x$	6.0 – 6.43
d	$y = 4.599 + 0.104x$	8.15 – 8.55
e	$y = 6.667 + 0.0707x$	10.3 – 10.5

masked, so that the two lines above and below 4% HCl approach a straight line (line d, Figure 2). (Above a definite concentration of KCl the water distribution appears to be a function of HCl concentration only).

Figures 3 and 4 express the relationship between the concentration of the acid in the solvent layer and its concentration in the aqueous layer (at various concentrations of KCl) as well as the dependence of the HCl content of the solvent layer on the KCl concentration of the aqueous solution. At small concentrations of acid in the aqueous layer, a small increase of KCl will cause a remarkable incerase in HCl in the alcohol; this effect is less apparent at higher concentrations of HCl in the water layer. Point A Figure 3 signifies the limit of liquid heterogeneity in the ternary system HCl-nBuOH-$H_2O^{5,6}$.

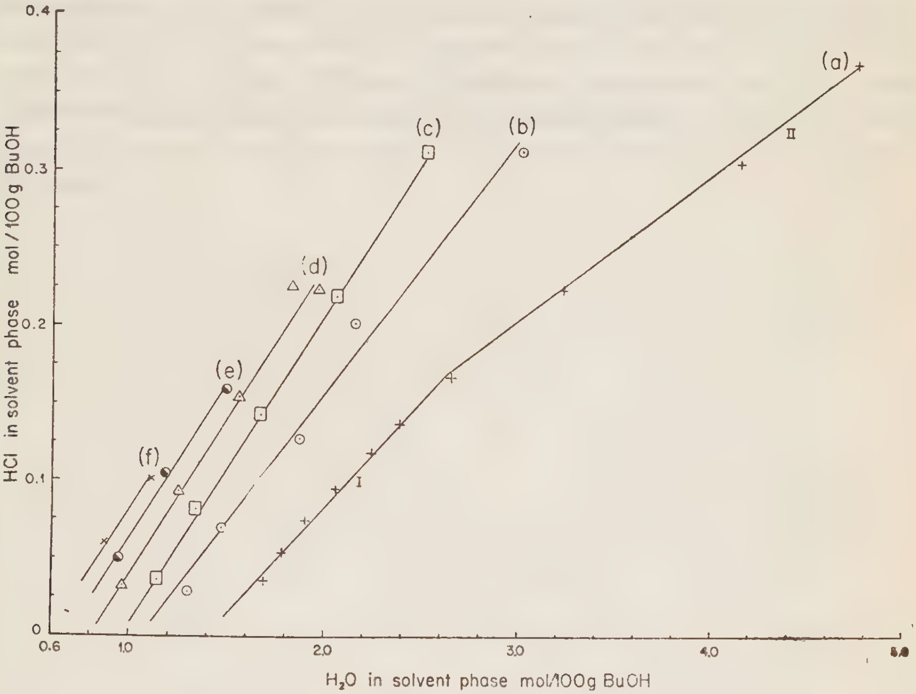

Figure 5

Line	Equation	KCl in aq. phase wt %
aI	$y = -0.187 + 0.136\,x$	0
aII	$y = -0.0879 + 0.0975x$	
b	$y = -0.1795 + 0.169\,x$	4.1 – 4.66
c	$y = -0.189 + 0.201\,x$	6.72 – 9.06
d	$y = -0.155 + 0.202\,x$	11.5 – 13.3
e	$y = -0.132 + 0.198\,x$	15.5 – 17.3
f	$y = -0.117 + 0.204\,x$	18.5 – 22.5

The points for zero concentrations of KCl in the aqueous phase (Figure 4) are given for the various HCl concentrations, for comparison. An attempt was made to see whether there is a definite relationship between the amounts of acid and water that pass into the alcoholic layer (Figure 5). This was done by plotting mole concentrations in the solvent phase on rectangular coordinates. At zero concentration of KCl in the aqueous layer this relation is represented by two intersecting straight lines; from ~5% and up to 22% a family of parallel lines expresses the dependence that exists between the amounts of HCl and H_2O transferred to the alcoholic layer; this seems to indicate the extraction of a definite hydrated species into the solvent phase, with a molar ratio of 1 HCl to 5 H_2O. Concentration from zero to ~5% KCl in the aqueous phase can be considered as a zone of transition such that the slope of the lines representing the relationship between HCl and H_2O in the solvent phase changes gradually.

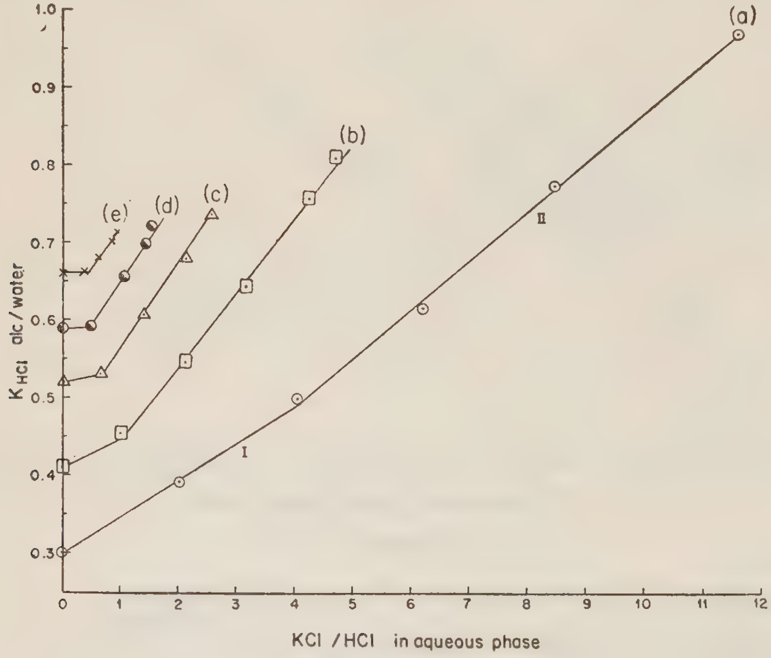

Figure 6

Line	Equation	HCl in aq. phase wt %	
aI	$y = 0.298 + 0.0498x$		1.94 – 2.3
aII	$y = 0.231 + 0.0639x$		
b	$y = 0.346 + 0.097x$	b	3.95 – 4.44
c	$y = 0.455 + 0.108x$	c	6.0 – 6.43
d	$y = 0.530 + 0.1225x$	d	8.15 – 8.55
e	$y = 0.605 + 0.116x$	e	10.3 – 10.5

Figure 6 shows the dependence of the distribution coefficient of HCl, on the ratio of KCl: HCl in the aqueous layer, for various levels of HCl in the aqueous phase. This relationship can be represented by two intersecting straight lines one of which is nearly horizontal (for concentrations of HCl in the aqueous phase down to about 4%).

Figure 7 is an attempt to represent the relations in the system in a more general form: it shows the dependence of the mole ratio of HCl to H_2O in solvent phase upon the weight ratio of KCl to HCl in the aqueous phase for different HCl concentrations in the aqueous layer. At all concentrations of HCl in the aqueous layer this relationship can be represented by straight lines on rectangular coordinates, but the slope of the lines increases with increasing concentration of HCl in the aqueous phase.

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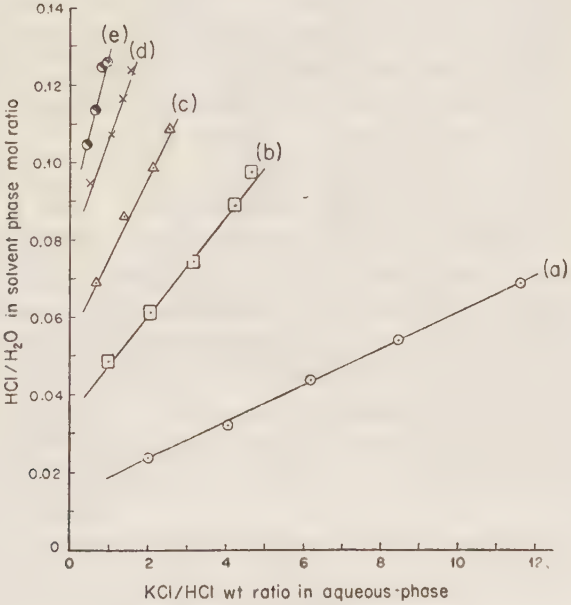

Figure 7

Line	Equation	HCl in aq. layer wt %
a	$y = 0.014 + 0.00477x$	1.94 – 2.3
b	$y = 0.0348 + 0.013x$	3.95 – 4.44
c	$y = 0.056 + 0.020x$	6.0 – 6.43
d	$y = 0.0776 + 0.0289x$	8.15 – 8.55
e	$y = 0.089 + 0.041x$	10.3 – 10.5

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TABLE I

Distribution of components in the system KCl—HCl—H_2O—nBuOH, at 30°C

	Solvent Phase wt%					Aqueous Phase wt%			K_{HCl} alc./aq.
No.	HCl	KCl	H_2O	BuOH	S.G.	HCl	KCl	S.G.	
1	0.905	0.129	18.8	80.16	0.8501	2.3	4.66	1.0253	0.394
2	1.09	0.12	16.6	82.19	0.8319	2.18	8.85	1.0557	0.50
3	1.31	0.145	14.6	83.94	0.8277	2.12	13.2	1.0863	0.618
4	1.58	0.18	14.2	84.04	0.8236	2.04	17.3	1.1166	0.775
5	1.88	0.217	13.3	84.6	0.8300	1.94	22.5	1.1488	0.97
6	2.02	0.14	20.5	77.36	0.8444	4.44	4.46	1.0346	0.455
7	2.34	0.21	18.8	78.65	0.8532	4.29	9.06	1.0658	0.545
8	2.69	0.22	17.8	79.28	0.8550	4.19	13.3	1.0963	0.644
9	3.07	0.27	17.0	79.66	0.8480	4.05	17.2	1.1252	0.757
10	3.2	0.31	16.1	80.39	0.8478	3.95	18.5	1.1345	0.81
11	3.4	0.186	24.2	72.21	0.8626	6.43	4.42	1.0433	0.53
12	3.85	0.293	22	73.86	0.8522	6.35	8.9	1.0747	0.606
13	4.2	0.292	20.9	74.6	0.8560	6.18	13.15	1.1038	0.68
14	4.41	0.304	20.1	75.2	0.8560	6.0	15.5	1.1220	0.735
15	5.07	0.24	26.3	68.39	0.8718	8.55	4.4	1.0509	0.594
16	5.53	0.435	25.3	68.73	0.8745	8.41	9.04	1.0843	0.656
17	5.8	0.39	24.4	69.41	0.8684	8.3	11.5	1.1001	0.699
18	5.88	0.39	23.3	71.43	0.8678	8.15	12.4	1.1080	0.722
19	6.96	0.392	32.5	60.15	0.8908	10.5	4.1	1.0557	0.664
20	7.14	0.54	30.8	61.52	0.8869	10.5	6.72	1.0754	0.68
21	7.28	0.635	28.6	63.5	0.8845	10.4	8.76	1.0872	0.70
22	7.35	0.61	28.7	63.34	0.8838	10.3	9.55	1.0941	0.714
23	Nil	Not determined	20	80		Nil	0.0		
24			15.5				7.6		
25			14.8				9.4		
26			13.5				12.8		
27			11.3				19.6		

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METAL KETYLS AS INITIATORS OF POLYMERISATION OF VINYL MONOMERS. POLYMERISATION OF ACRYLONITRILE, STYRENE AND METHYL METHACRYLATE BY DISODIUM BENZOPHENONE

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The anionic polymerisation of acrylonitrile, styrene and methyl methacrylate by disodium benzophenone in tetrahydrofuran was investigated. The effects of concentration of catalyst and monomer were studied. The mechanism of the polymerisation is discussed.

In continuation of our work on the polymerisation of vinyl monomers by monosodium benzophenone[1,2], we studied the polymerisation of acrylonitrile, styrene and methyl methacrylate using disodium benzophenone. Owing to its having both a carbanion and an alkoxide group in its molecule, the latter compound can be expected to have outstanding properties as initiator. Such dialkali metal ketyls have not been used up to now as initiators of polymerisation of these monomers.

Polymerisation of acrylonitrile

This was investigated in tetrahydrofuran solution in which the monomer is soluble. The polymer, being insoluble, precipitated on formation.

The dependence of yield and molecular weight of polyacrylonitrile on the amount of the catalyst was investigated. Experiments were carried out (Table I) with identical quantities and concentrations of acrylonitrile, the monomer being added with stirring in one portion to the disodium benzophenone prepared in tetrahydrofuran. The yield increased with increasing amount of catalyst to approximately quantitative values. The molecular weights of the polyacrylonitriles obtained did not depend on the amount of catalyst.

The dependence of molecular weight on the concentration of monomer was studied under otherwise constant conditions (Table II). The molecular weight was independent of the concentration of the monomer.

Polymerisation of styrene

The polymerisation of styrene (having no α-hydrogen atom available for chain transfer) was significantly different in several aspects from that of acrylonitrile. The dependence of yield and of molecular weight on the amount of catalyst was investigated, under otherwise constant conditions (Table III). The yield was quantitative even for low amounts of catalyst. The molecular weight decreased with

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increasing amount of catalyst, the decrease not being directly proportional to the amount of catalyst. In most cases the purple-violet colour of the solution due to the catalyst was retained to the end of the polymerisation showing that not all the catalyst took part in the polymerisation process.

The dependence of yield and molecular weight of styrene on the amount of monomer was investigated under comparable conditions (Table IV). The yield was quantitative for all concentrations of monomer. The molecular weight increased with increasing monomer concentration, the increase being not directly proportional to the amount of monomer.

Polymerisation of styrene by disodium benzophenone was also effective at low temperature (–60°), the molecular weight obtained being greater than on polymerisation at 0°.

Polymerisation of methyl methacrylate

This was in several aspects similar to that of styrene. The dependence of yield and molecular weight of poly(methyl methacrylate), on the amount of disodium benzophenone catalyst was investigated under otherwise constant conditions (Table V). The yield increased with increasing amount of catalyst, while the molecular weight decreased with increasing amount of catalyst, the decrease being small at the higher concentrations of catalyst. The molecular weights obtained here were higher than in the case of polyacrylonitrile.

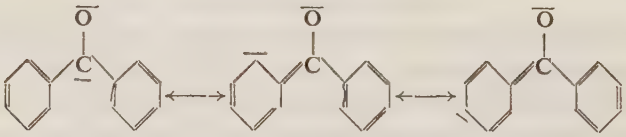
As regards the dependence of molecular weight of the poly (methyl methacrylate) on the amount of monomer (Table VI), it increased with concentration of monomer, the increase not being directly proportional to the amount of monomer.

Disodium benzophenone polymerised methyl methacrylate also at very low temperature (–60°), contrary to the action of monosodium benzophenone[2]. The molecular weight increased with lowering in temperature.

DISCUSSION

Initiation

Disodium benzophenone possesses a carbanion as well as an alkoxide group; the carbanion can be stabilised by seven resonating structures such as:



In the previous paper[2] we have shown that the polymerisation of acrylonitrile and methyl methacrylate by monosodium benzophenone was initiated by the alkoxide. In the case of disodium benzophenone, the carbanion is a strong base so that it seems quite possible that initiation of polymerisation of these two monomers is both by the alkoxide and the carbanion. Infrared spectra of the polyacrylonitriles and poly (methyl methacrylates) showed absorptions at 8.8–9.3 μ (dialkyl ether) and at 13–13.2 μ and 14.1 μ (mono-substituted benzene).

As monosodium benzophenone alone was not effective[2], the polymerisation of methyl methacrylate at −60° seems to be mostly initiated by the carbanion of the disodium benzophenone.

In the polymerisation of styrene, monosodium benzophenone is a very weak catalyst[1], and only traces of polymer were formed. On the other hand, disodium benzophenone is a very strong catalyst even at very low temperature (−60°). The initation in this case is through the carbanion which is a stronger base than the alkoxide. This was confirmed by the infrared spectra of the polystyrenes which showed absorption bands at 2.9–2.95 μ (hydroxyl groups).

It may be mentioned that in a preliminary work[3] on the polymerisation of styrene by sodium benzophenone, it was noted that styrene only polymerised in the presence of excess sodium metal; however, the nature of the initiation was not explained. From the present work it appears that the polymerisation was due to the formation of disodium benzophenone from monosodium benzophenone and sodium.

Termination

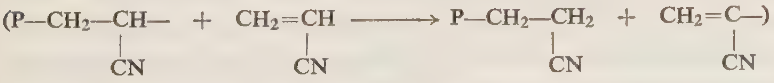
Regarding termination, the polymerisation of acrylonitrile was different from that of styrene and of methyl methacrylate. We have shown that with acrylonitrile the molecular weight was independent of both monomer and catalyst. Also infrared spectra of the polyacrylonitriles showed absorption bands at 5.9–6.1 μ for ($CH_2=$) terminal double bonds[4]; this is consistent with the assumption that termination is by chain transfer to monomer which has a reactive α-hydrogen atom as can be seen from the following scheme of polymerisation steps:

Initiation $C + M \xrightarrow{\mathrm{ki}} CM^-$

Propagation $CM^- + M \xrightarrow{\mathrm{kp}} CMM^-$

Termination $CM_n^- + M \xrightarrow{\mathrm{kt}} CM_nH + M^-$

The degree of polymerisation, assuming termination by chain transfer to monomer,



$$(P{-}CH_2{-}\underset{\large CN}{\underset{|}{CH}}{-} + CH_2{=}\underset{\large CN}{\underset{|}{CH}} \longrightarrow P{-}CH_2{-}\underset{\large CN}{\underset{|}{CH_2}} + CH_2{=}\underset{\large CN}{\underset{|}{C}}{-})$$

would be equal to $\dfrac{\mathrm{kp}\ [M]\qquad [CM_n^-]}{\mathrm{kt}\ [M]\qquad [CM_n^-]} = \text{constant.}$

The molecular weights of the polyacrylonitriles obtained on polymerisation by either disodium or monosodium[2] benzophenone in tetrahydrofuran are of the same order, showing that the catalyst type, whether alkoxide or carbanion, has no bearing on the molecular weight and that on using the same solvent (same dielectric constant) the molecular weight of the polymers is the same.

Termination of anionic polymerisation can occur by addition of a proton to the propagating anion. In the case of the polymerisation of styrene and of methyl methacrylate, the polymerisation mixture contained tetrahydrofuran, monomer and disodium benzophenone, none of which is able to donate a proton for termination. Furthermore the styryl carbanions are resonance-stabilized by the benzene ring and four resonance structures are possible[5]. In the case of "living" polystyrene obtained by polymerisation with sodium naphthalene, it was shown[6,7] that the molecular weight is directly proportional to the monomer concentration and inversely proportional to the catalyst, (D.P. $= \frac{[M]}{\frac{1}{2}[C]}$), and independent of temperature. In the polymerisation of styrene we found that the molecular weight increased with concentration of monomer and decreased with catalyst concentration, but the decrease was not directly proportional. Also the molecular weight of the polymers was temperature dependent.

We have found that even after complete polymerisation of the styrene unconsumed catalyst was present as seen from the purple-violet colour of the polymerisation solution. This shows that not all catalyst molecules start polymerisation and that the monomer adds more readily to a growing styrene carbanion than to catalyst[8]. For this reason the molecular weights of the polystyrenes obtained do not depend linearly on the amount of catalyst. It is also possible that at higher temperature more catalyst would participate in the initiation process causing lowering in molecular weight.

Proof for the existence of "living" polystyrene was obtained from experiments in which acrylonitrile was added to a polymerisation mixture of styrene, at the end of the polymerisation, and was polymerised completely. The mixture obtained of polystyrene and polyacrylonitrile on fractionation from different solvents gave a small fraction of a block polymer of styrene and acrylonitrile containing about 80% acrylonitrile and 20% styrene. Besides differences in solubility, infrared spectra of the block polymers showed the absorptions of both the nitrile group of the polyacrylonitrile at 4.4 μ and of polystyrene at 6.2 μ, 13.4 μ and 14.2 μ.

This shows that carbanion propagation centres, still intact, of polystyrene were present. The relatively small amount of block polymer and large amount of free polyacrylonitrile obtained is due to the fact that the polymerisation mixture contained excess catalyst which did not enter the polymerisation, and most of the acrylonitrile was polymerised by this catalyst.

In the case of the polymerisation of methyl methacrylate, which has no α-hydrogen atom, the possibilities of termination may be similar to that of styrene. The infrared spectra showed no absorption at 6–6.1 μ for terminal ($CH_2=$) double bonds[4]. The molecular weight was found to increase with concentration of monomer and decrease with concentration of catalyst.

These factors were discussed in the previous paper[2].

EXPERIMENTAL

Materials

Tetrahydrofuran was dried over sodium hydroxide, refluxed over sodium wire, distilled and boiled under nitrogen before use. Acrylonitrile was purified according to Bamford and Jenkins[9] by successive washings with dilute sulphuric acid (5%) dilute sodium carbonate (5%) and water. After drying thoroughly on calcium chloride it was fractionally distilled at atmospheric pressure and stored in the dark over calcium chloride. Immediately before use, it was filtered and fractionally distilled *in vacuo* under nitrogen, the middle fraction, about 70%, being used, Methyl methacrylate was dried over sodium sulphate; before use, it was fractionally distilled under nitrogen at atmospheric pressure and then *in vacuo*; the middle fraction, about 70%, was used. Styrene (B.D.H.) was dried over anhydrous calcium chloride and distilled from sulphur under nitrogen. Before use it was fractionally distilled *in vacuo*, the middle fraction only, about 70%, being retained. Benzophenone (B.D.H.), m.p. 47-8°, was dried in a vacuum desiccator. Toluene was dried over sodium and distilled. Dimethylformamide was fractionally distilled. Nitrogen was freed from oxygen by passage through a quartz tube containing fresh copper wire at 600°, then through a 5% alkaline permanganate solution followed by a solution of 20% pyrogallol in 20% sodium hydroxide, and dried over concentrated sulphuric acid.

Preparation of disodium benzophenone

The preparation of catalyst and the polymerisations were carried out under oxygen-free nitrogen. Benzophenone (0.2 mole) dissolved in tetrahydrofuran (600 ml) and sodium (0.6 mole) (excess) in the form of wire 0.5 mm diameter obtained from sodium press, were shaken in a shaking machine in a flask fitted with a self-sealing rubber cap. The purple-violet colour of the disodium benzophenone appeared in 20–30 min; shaking was continued for 8 hrs and the reaction mixture was left overnight. The catalyst was filtered under nitrogen into a bottle fitted with a rubber gasket. Freshly prepared catalyst was used in all polymerisation reactions, and its concentration was checked by titration with hydrochloric acid (0.1N) before use.

Polymerisation of monomers

The polymerisations were carried out in three-necked flasks fitted with high speed stirrer, a gas-adapter for introducing nitrogen and a thermometer. Monomer was added in one portion under stirring to the required amount of disodium benzophenone measured by syringe, dissolved in tetrahydrofuran and cooled to the required polymerisation temperature. The polymerisation was stopped after the required time by adding 20 ml of cold concentrated hydrochloric acid in methanol (1:1). Polyacrylonitrile was filtered off, washed with dilute hydrochloric acid, water, methanol and ether to remove benzophenone and monomer and dried to constant weight in an electric oven at 60°. Polystyrene and poly(methyl methacrylate) were precipitated from their solutions in tetrahydrofuran by methanol. The polymers were left under methanol until complete solidification, then filtered, washed with methanol, hydrochloric acid, water and methanol, followed by stirring for several hours with methanol to remove any traces of adhering monomer and finally dried in vacuum desiccator.

All polymerisation experiments were checked for reproducibility.

Polymer samples were further purified and dried for molecular weight determinations. Viscosities of polymer solutions were measured in an Ostwald viscosimeter.

Preparation of a block polymer of styrene-acrylonitrile

Styrene (10 ml) was polymerised according to Table III using 3 mmole catalyst. After 30 min acrylonitrile (10 ml) was added to the polymerisation mixture, which had a violet colour from excess catalyst, and was polymerised. After 20 min another 10 ml of acrylonitrile were added and the polymerisation was stopped after 30 min. 25 g polymer were obtained (quantitative yield). Polymer (5 g) was fractionated by consecutive extractions with boiling solvents; three times with benzene and twice with acetone, using 100 ml solvent for each extraction. The benzene extract (1.6 g) was pure polystyrene. The small acetone extract was further extracted with boiling benzene (100 ml), and also triturated with boiling benzene to remove any adhering polystyrene. 0.3 g polymer was thus obtained which contained 21% nitrogen showing it to consist of 80% polyacrylonitrile and 20% polystyrene. The block polymer starts sintering at 170–175° and decomposes at *ca.* 220°, which is lower than pure polyacrylonitrile.

A duplicate experiment gave essentially the same results.

TABLE I

Polymerisation of acrylonitrile. Dependence of yield and molecular weight on the amount of catalyst. Experimental conditions. Acrylonitrile (5 ml; 1 mole/l/) was added in one portion to disodium benzophenone in tetrahydrofuran (70 ml). Polymerisation temperature 0°, time 30 min.

Catalyst (mmole)	6.5	13	20	26	40
[Catalyst] (mole/l)	0.087	0.174	0.267	0.347	0.534
Polymer (g)	2.7	3.5	4	4	4
Yield (%)	68	88	100	100	100
[η] dl/g)	0.146	0.145	0.143	0.143	0.143
10^{-3} M*	5.4	5.3	5.2	5.2	5.2

* Average molecular weights of the polymers were calculated from intrinsic viscosities measured in dimethylformamide at 30° by use of the equation[10] $[\eta] = 2.33 \times 10^{-4} M^{0.75}$.

TABLE II

Polymerisation of acrylonitrile. Dependence of molecular weight on amount of monomer.

Experimental conditions. Acrylonitrile was added in one portion to disodium benzophenone (0.026 mole; 0.52 mole/l) in tetrahydrofuran.The total volume of solvent and monomer was kept constant (50 ml). Polymerisation temperature 0°, time 30 min.

Monomer (ml)	2	4	5	7	10
[Monomer] (mole/l)	0.6	1.2	1.5	2.1	3
Polymer (g)	1.6	3	4	5.6	7.5
Yield (%)	100	94	100	100	94
$[\eta]$ (dl/g)	0.15	0.145	0.143	0.15	0.143
10^{-3}M	5.6	5.3	5.2	5.6	5.2

TABLE III

Polymerisation of styrene. Dependence of yield and molecular weight on amount of catalyst.

Experimental conditions. Styrene (5 ml; 0.88 mole/l) was added in one protion to disodium benzophenone prepared in tetrahydrofuran (45 ml). Polymerisation temperature 0°, time 30 min.

Catalyst (mmole)	0.8	1.7	2.6	5.2*
[Catalyst] (mole/l)	0.016	0.034	0.052	0.104
Polymer (g)	4.5	4.5	4.5	4.5
Yield (%)	100	100	100	100
$[\eta]$ (dl/g)	0.17	0.13	0.1	0.064
10^{-3}M**	23.5	15.8	11	6

* Using monomer (10 ml) and polymerisation temp. (–60°) under otherwise constant conditions gave 9 g (100%) of polymer; $[\eta] = 0.19$ dl./g; M = 26,500.

** Average molecular weights of the polymers were calculated from intrinsic viscosities, measured in benzene at 25°, by use of the equation[11] $[\eta] = 1.12 \times 10^{-4} M^{0.73}$.

TABLE IV

Polymerisation of styrene. Dependence of yield and molecular weight on amount of monomer.

Experimental conditions. Styrene was added in one portion to disodium benzophenone (2.3 mmole; 0.046 mole/l) prepared in tetrahydrofuran; the total volume of solvent and monomer was kept constant (50 ml). Polymerisation temperature 0°, time 30 min.

Monomer (ml)	2	4	6	8	10
[Monomer] (mole/l)	0.35	0.7	1.05	1.4	1.75
Polymer (g)	1.8	3.6	5.4	7.2	9
Yield (%)	100	100	100	100	100
$[\eta]$ (dl/g)	0.064	0.092	0.105	0.115	0.14
10^{-3}M	6	9.8	11.8	13.3	17

TABLE V

Polymerisation of methyl methacrylate. Dependence of polymerisation yield and molecular weight on amount of catalyst.

Experimental conditions. Methyl methacrylate (10 ml; 2.34 mole/l) was added in one portion to disodium benzophenone prepared in tetrahydrofuran (30 ml). Polymerisation temperature 0°, time 30 min.

Catalyst (mmole)	0.6	2.4	8.25*
[Catalyst] (mole/l)	0.015	0.06	0.206
Polymer (g)	3	8	8
Yield (%)	32	85	85
[η] (dl/g)	0.12	0.092	0.079
10^{-3} M**	37	25.4	20.5

* Using catalyst (11 mmole; 0.22 mole/l) in tetrahydrofuran (50 ml) and polymerisation temp. (–60°) under otherwise constant conditions gave 9 g (96%) of polymer; [η] =0.115 dl/g; M = 34,500.

** Average molecular weights of the polymers were calculated from intrinsic viscosities, measured in toluene at 30°, by use of the equation[12] $[\eta] = 6.87 \times 10^{-5} M^{0.71}$.

TABLE VI

Polymerisation of methyl methacrylate. Dependence of yield and molecular weight on amount of monomer.

Experimental conditions. Methyl methacrylate was added in one portion to disodium benzophenone (2.4 mmole; 0.048 mole/l) prepared in tetrahydrofuran. The total volume of solvent and monomer was kept constant (50 ml). Polymerisation temperature 0°, time 30 min.

Monomer (ml)	2	10	20
[Monomer] (mole/l)	0.375	1.87	3.75
Polymer (g)	1.8	8.5	17
Yield (%)	100	90	90
[η] dl/g)	0.067	0.094	0.14
10^{-3} M	16.2	26	46

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ORGANIC FLUORINE COMPOUNDS. PART XVIII.[1]

The Reaction of Diethyl Oxalofluoroacetate with Aromatic Hydrocarbons

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α-Keto acids and their esters react with aromatic hydrocarbons (or their derivatives) in the presence of sulphuric acid (or aluminium chloride) by either of the following two mechanisms: addition to the carbonyl double bond to form α-hydroxy-α-arylated acids or esters, and further replacement of the tertiary hydroxyl group by a second aryl radical, thus yielding α, α-diarylated acids or esters [2-6]. No experiments appear to have been carried out with ethyl oxaloacetate.

It seemed of interest to study the behaviour of diethyl oxalofluoroacetate. The α-carbonyl group is replaced by two aryl radicals, e.g. in the case of toluene:

$$\begin{aligned}&\text{EtOOC.CO.CHF.COOEt} + 2\text{C}_6\text{H}_5\text{CH}_3 \longrightarrow\\&\qquad\text{EtOOC.C.(C}_6\text{H}_4\text{.CH}_3)_2\text{.CHF.COOEt}\end{aligned}$$

The *para*-position of toluene enters into the reaction. Oxidation of the diethyl ester obtained with chromic acid led to benzophenone-4,4′-dicarboxylic acid, which was identified as the known dimethyl ester.

Diethyl α-fluoro-β, β-di-(p-tolyl)-succinate. Toluene (5g) was added slowly to a solution of diethyl oxalofluoroacetate (5g) in concentrated sulphuric acid (20g) at a temperature not exceeding 45°. After 12 hours, the reaction product was poured onto ice and extracted with toluene. The solution was then treated with sodium hydrogen carbonate solution, dried and concentrated in a vacuum of 30 mm. The *product* distilled at 182-184° (0.1 mm); the yield was quantitative (9g). (Found: C, 71.0; H, 6.5; F, 5.1; OC_2H_5, 23.9 $C_{22}H_{25}FO_4$ requires C, 71.0; H, 6.7; F, 5.1; OC_2H_5, 24.2 %).

α-Fluoro-β,β-di-(p-tolyl)-succinic acid. A mixture of the foregoing ester (5g), glacial acetic acid (15 ml) and 48 % hydrobromic acid (5 ml) was refluxed for one hour and after addition of water (5 ml) for an additional hour. The solution was poured into 100 ml of water and the solid filtered off and re-precipitated with acid from its solution in sodium hydrogen carbonate solution. The acid which crystallizes with water and melts in this form at 70–75°, was dissolved in benzene and, after removal of the water by azeotropic distillation and concentration of the solution, brought to crystallisation by addition of low-boiling (40–60°) petroleum ether. M.p. 124°.

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(Found: C, 68.1; H, 5.7; F, 6.0. $C_{18}H_{17}FO_4$ requires: C, 68.4; H, 5.4; F, 6.0%). *Oxidation.* To a solution of diethyl α-fluoro-β, β-di-(*p*-tolyl)-succinate (4g) in glacial acetic acid (50 ml), chromic anhydride (10g) and then a mixture of concentrated sulphuric acid (5g) and water (10 ml) was added slowly and with stirring, so that the temperature did not rise above 60°. The stirring was continued for 3 hours and the mixture kept at room temperature for 12 hours and poured into water. The precipitate was filtered, extracted with sodium hydroxide solution (most of it was soluble) and precipitated again by addition of hydrochloric acid. The *product* was recrystallized from glacial acetic acid and melted above 300°, as indicated[7] for benzophenone - 4,4′ - dicarboxylic acid. For identification it was transformed into its *dimethyl ester*, which—after recrystallization from ethanol—melted at 230° (lit.[7]: 224; 231°).

Whilst the reaction with toluene sets in at 35–40°, that with benzene begins only at 45°. On the other hand, naphthalene reacts already at 25–30°. In all cases, the reaction is slightly exothermic.

This study has been carried out under a grant of the U.S. National Institutes of Health.

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SPECIFIC IONIC EFFECTS ON REACTION RATES: THE REACTION BETWEEN BROMOACETATE AND HYDROXYL IONS

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ABSTRACT

The specific effect of the cation on the rate of a reaction between two anions has been demonstrated for the case of the reaction between bromacetate and hydroxyl ions. The accelerating effect of the added salt increases in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (as in previous cases) and $Sr^{++} < Ba^{++}$. On the other hand, at constant sodium ion concentration, the rate constant is not influenced by a change of the ionic strength achieved by changing the valency of the *anion*. The plots of the logarithm of the rate constant *vs.* cation concentration all exhibit an initial steep rise, which gradually flattens out and at $M \cong 0.5$ becomes linear. Energies of activation in the presence and absence of added salts were determined.

INTRODUCTION

The specific ionic effect of the *cation* of an inert salt on a reaction taking place between two *anions* has recently been the subject of several experimental investigations and theoretical discussions.[1,2,3,4] Further experimental evidence in this direction seemed however desirable. In a quest for a simple, well-known second order reaction between anions we chose the reaction between bromoacetate and hydroxyl ions, which yields bromide and glycolate ions. This reaction was investigated by Dawson and Dyson[5] who found that in addition to the reaction between bromoacetate and OH^-, the reaction between bromoacetate and other bases, such as H_2O, bromoacetate, glycolate, acetate and formate has to be considered. The first reaction, however, has a rate-constant which is almost 1000 times greater than the others. Therefore, in the presence of a reasonable amount of OH^- we may consider the hydrolysis to proceed purely by

$$CH_2BrCOO^- + OH^- \longrightarrow CH_2OHCOO^- + Br^- \qquad (1)$$

EXPERIMENTAL

The bromoacetic acid was B. D. H. (Laboratory Reagent); solutions were prepared by weighing the desired amount, checking the concentration with standard alkali solution and adding sodium hydroxide to obtain sodium bromoacetate. All other reagents were either Baker's Analyzed or May and Baker "suitable for analysis".

The progress of the reaction was followed either argentometrically (Volhard),

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titrating the Br^- which is formed, or acidimetrically (using phenolphtalein), titrating the OH^- which disappears.[5]

The reaction was carried out in "Low-Actinic" glass-stoppered Erlenmeyer flasks in order to avoid photochemical decomposition. Unless otherwise stated the temperature was 59.5°. The reactants were always present in the form of their sodium salts.

No special precaution was taken to purify the NaOH solution from carbonate.The carbonate-concentration was however determined for every experiment, and corrected for. This may introduce a certain error since $CO_3^=$, like other ions of weak acids[5], was found to exert an accelerating effect (see below). Since the carbonate-concentration was never more than a few percent of the hydroxyl ion concentration, the error is probably negligible.

RESULTS

1. *Check of mechanism.* (a) One experiment where 3.5 M $NaNO_3$ had been added, was followed both by the argentometric and the acidimetric method. The agreement between the two methods was satisfactory. This shows[5] that mechanism (1) is indeed operative. (In most of the experiments described below the argentometric method was used since it was found to be more sensitive.) (b) In the presence of 1 M $NaNO_3$, the concentrations of the reactants were varied from 0.0062 to 0.0155 for bromoacetate, and from 0.028 to 0.058 for OH^-. The second-order rate constant showed no trend with the concentration of the reactants which further proves mechanism (1).

2. *Rate-constant at low salt concentration.* In the absence of foreign salt the total concentration of the reactants was varied between 0.069 to 0.017; as expected, the rate constant k decreased with decreasing concentration. However, at still lower concentrations, the values of k started increasing again. This tendency was particulary pronounced when the hydroxyl ion concentration was very low. For instance, when the total concentration was 7.3×10^{-3} M, we found $k = 1.47\times10^{-3}$ mol^{-1} l sec^{-1} using $[CH_2BrCOO^-] = 2.8\times10^{-3}$ M and $[OH^-] = 4.5\times10^{-3}$ M, and $k = 2.45\times10^{-3}$ mol^{-1} l sec^{-1} using $[CH_2BrCOO^-] = 5.1\times10^{-3}$ and $[OH^-] = 2.2\times10^{-3}$ M. This effect is due to the fact that at very low hydroxyl ion concentration the reaction between water and bromoacetate[5] makes an appreciable contribution to the total rate. We therefore did not attempt to investigate reaction (1) at very low ionic strength, which might have enabled us to determine whether under those conditions it obeys the Debye Limiting Law, and to evaluate the rate constant at infinite dilution.

In the following experiments, the concentrations of the reactants were within the the limits mentioned in section 1 in the case of Na^+, and within somewhat narrower limits in the case of the other cations; the foreign salts were added to this reaction mixture.

3. *Influence of anions, and of ionic strength.* When 0.5 M and 1 M sodium ions were added in the form of nitrate and sulfate, the rate-contants were found to be identical — within the limits of experimental error — for identical sodium ion concen-

trations, although the ionic strength is 0.5 and 0.75, and 1.0 and 1.5 respectively. Acetate was found to have a slight accelerating effect, and carbonate a very pronounced one.

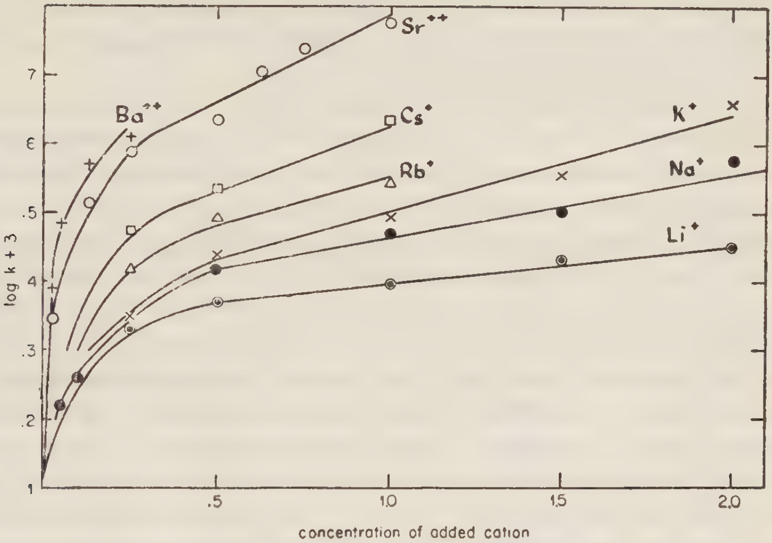

Figure 1
The logarithm of the rate constant as a function of the concentration of added salt, for seven different cations

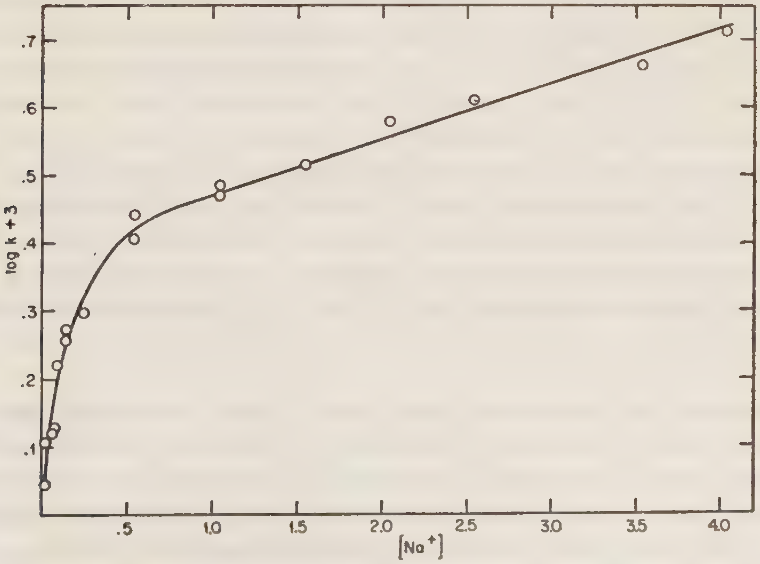

Figure 2
The logarithm of the rate constant as a function of the total sodium ion concentration

4. *Influence of the concentration and of the nature of the cation of added salts.* All the salts were employed in the form of their nitrates, except for the use of rubidium and caesium sulphates. The results are shown in Figure 1 where the logarithm of the rate constant is plotted against the concentration of the added cation. For the case of sodium where concentrations up to 4 M were employed, Figure 2 shows the dependence of log k on the total salt concentration.

5. *Energy of Activation.* The apparent energy of activation was calculated from experiments carried out at 59.5 and 78.6°. In the absence of added salts, its value was 23.0 kcal mol^{-1}. In the presence of salts, it was definitely lower. However, when we investigated the influence of the *concentration* of a given cation, or the influence of various *cations* at a given concentration, we found that any trend with either of these variables was within the limit of experimental error. The cations and concentrations employed were Li^+ (0.25 and 2M), Na^+ (0.25 and 3.5 M), K^+ (0.25 and 2M) and Cs^+ (0.25 M). The mean value for the seven pairs of experiments was 19.2 ± 1.8 (maximum deviation) kcal mol^{-1}.

The lack of correlation between salt-concentration and apparent energy of activation parallels our previous findings[1]. The fact that the addition of inert salts decreases the apparent energy of activation contradicts the arguments of Moelwyn-Hughes[6] and of La Mer[7] but seems to be in agreement with the findings of Indelli and Amis[4] for the reaction between persulfate and iodide, and has been discussed in detail by these authors. In view of the quality of our own measurements a detailed theoretical discussion does not seem justified in the present case.

DISCUSSION

Our results show that this reaction between two ions of like sign exhibits a considerable positive salt-effect. However, it is not the ionic strength as such which influences the rate of the reaction. This can be seen by comparing the effect of sodium nitrate with that of sodium sulfate. The two salts have an identical effect at the same sodium ion concentration, and not at the same ionic strength.

All the curves of log k *vs.* concentration show the same general picture: an initial sharp rise in the rate constant gradually flattens out, and at concentrations above $\sim$0.5 M we get a linear relationship. This linear part corresponds to previous findings[1,8] whereas the low-concentration range could not be investigated in the hypobromite decomposition, where an excess of alkali hydroxide has to be present. The non-linear part is in agreement with the results of Indelli and Prue[2] for the iodide persulfate reaction.

Furthermore, the various salts exhibit *specific* effects. The specific effects of the anions can readily be explained by the assumption of reactions parallel to reaction (1).[5] The specific effect of the alkali cations increases in the same order as in the hypobromite decomposition[1] (except that the influence of Cs^+ is now definitely higher than, and not almost equal to that of Rb^+). A similar increase of the accelerating effect is observed with the alkaline earth metals on passing from Sr^{++} to Ba^{++}. (Unfortunately, Mg^{++} and Ca^{++} could not be investigated, since their hydroxides are not sufficiently soluble). These results can be explained on the same lines as in our previous paper[1]. The fact that the divalent ions have a very much stronger effect than the monovalent ones at equal concentrations is also in good agreement with the picture of the cation helping the two reacting anions to overcome their electrostatic repulsion. No *quantitative* conclusion connecting the rate-constant with the charge and the radius of the ion in solution seems however to be warranted at the present stage.

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AN APPROXIMATE TREATMENT OF THE KINETICS OF REVERSIBLE PARALLEL REACTIONS

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ABSTRACT

An approximate treatment of the kinetics of reversible reactions is given, where the back reaction is taken into account by using a suitably corrected time scale. The method is particularly appropriate for systems of parallel reactions, where the rate-constant may have to be evaluated by trial and error.

Let us consider a reaction in solution:

$$A \rightleftharpoons X + Y + \ldots. \tag{1}$$

which proceeds according to two or more parallel paths, *viz.*

$$B + A \overset{k_B}{\rightleftharpoons} B' + X + Y + \ldots. \tag{2}$$

$$C + A \overset{k_C}{\rightleftharpoons} C' + X + Y + \ldots. \tag{3}$$

where the concentrations of B, C, B′ and C′ are interconnected through some chemical equilibrium which is fast in comparison with reaction 1. One of the substances, say B, may be the solvent. In such cases the parallel reactions cannot be studied separately. At best it may be possible to find conditions where one of them, say reaction 2, can be isolated. After integration of the rate equation, a linear combination of k_C and k_B, (or, when it is possible to isolate reaction 2, the ratio k_B/k_C) then appears in a transcendental equation, and has to be evaluated by an appropriate trial and error method. Whereas this usually presents no special difficulty, the situation is more complicated when under the given experimental conditions the back reaction cannot be neglected. In that case — especially when several products X, Y ... are formed — the integrated form of the rate equation may become very cumbersome for use in a trial and error method.

When a reaction follows the scheme outlined above, it is possible to write the rate equation in the form :

$$\mathrm{d}x/\mathrm{d}t = (\text{rate of forward reaction}) \times (1 - \varphi) \tag{I}$$

(where x is the concentration of one of the products formed.)

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The expression "rate of forward reaction" is the *sum* of the forward rates of reactions 2 and 3 ; the meaning of φ is the ratio of the rate of the back reaction to that of the forward reaction. It usually starts from a negligibly small value at the beginning of the reaction and it reaches unity at the end. For every measured value of x_t, $\varphi(x_t)$ can easily be calculated. We may use, for instance, the expression

$$\varphi(x_t) = \frac{1}{K_2} \frac{\prod_j c_j}{\prod_i c_i} \tag{II}$$

where K_2 is the equilibrium constant of reaction 2, and the suffixes i and j refer, respectively, to the reactants and products of this reaction. However, since the equilibrium concentrations B, C, B′ and C′ are all interconnected, we shall get the same result if we express $\varphi(x_t)$ in terms of K_3 and the concentrations of the substances appearing in reaction 3. This is a consequence of the fact that the value of φ must be independent of the relative contributions of reaction 2 and 3 to the measured rate. Therefore, even if there exists an additional reaction — say between A and some substance D — which by mistake we may have failed to take into account when setting up the rate equation, the value of φ will not be affected, provided D and D′ are also in rapid equilibrium with B, C, B′ and C′.

The hydrolysis of chlorine in the presence of acetate represents an example of such a reaction scheme[1]. The reactions of chlorine with water, with acetate, and possibly with hydroxyl ions have to be taken into consideration.

In this case :

$$\varphi = \frac{K_a}{K_h} \frac{x^2\,([\mathrm{HAc}]_o + x)}{(a-x)\,([\mathrm{Ac}^-]_o - x)} \tag{III}$$

where K_h and K_a represent the hydrolysis constant of chlorine and the dissociation constant of acetic acid, respectively, a is the stoichiometric concentration of chlorine, and $[\mathrm{HAc}]_o$ and $[\mathrm{Ac}^-]_o$ are the concentrations of acetic acid and acetate when $x = 0$.

Now, we found that the following device greatly simplified the labour involved in integrating the rate-equation and especially in using the result for the calculation of k_B/k_C by trial and error[1].

When $\varphi(x_t)$ is plotted against time, simple curves are obtained which can conveniently be represented as power series, *viz.*

$$\varphi(x_t) = \varphi(t) = a_o + a_1 t + a_2 t^2 \tag{IV}$$

The coefficients can easily be calculated, for example by the method of least squares. When for the last value of x_t measured, φ is still very small, a linear expression was found to suffice. When it is comewhat larger (up to about 0.4) a quadratic expression was usually found to give a satisfactory fit.

Figure 1 shows φ as a function of time for three typical experiments[1]. The circles correspond to the values calculated from expression III for the measured values of x, whereas the smooth line represents analytical expressions of the type of expression IV. The fit is seen to be satisfactory.

Equation I is usually easily integrated when written in the approximate form:

$$\int_{x_0}^{x_t} \frac{\mathrm{d}x}{\text{(rate of forward reaction)}} = \int_0^t [1 - \varphi(t)]\,\mathrm{d}t$$

$$= t - (a_0 t + (a_1/2)t^2 + (a_2/3)t^3) \equiv \Theta \qquad \text{(V)}$$

Any trial and error method for calculating the best value of the left hand side of equation V may now be employed, where the right hand side represents a "corrected time" Θ and is used in the same way as ordinary time would be used in a case where the back reaction can be neglected.

The technical advantage of the method lies in the fact that $\varphi(t)$ appears in the numirator of the integrand on the right hand side, whereas in the integration of the exact form of equation I the expression $[1 - \varphi(x)]$ would appear in the denominator on the left hand side.

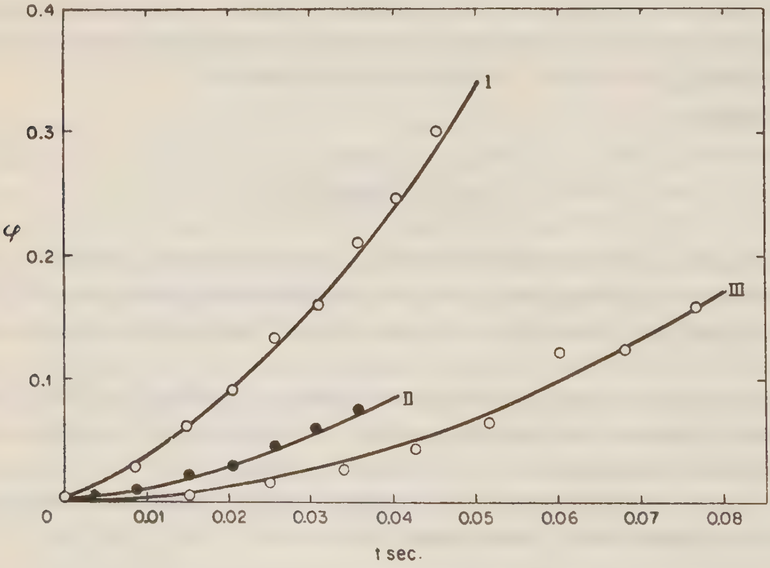

Figure 1

The expression φ as a function of time for 3 typical experiments. The circles represent experimental values of $\varphi(x_t)$; the smooth lines represent $\varphi(t)$ as power series, *viz.*

(I) $\varphi(t) = 0.003 + 2.8\,t + 80\,t^2$
(II) $\varphi(t) = 0.9\,t + 30\,t^2$
(III) $\varphi(t) = 27\,t^2$

The above method should be applicable to many other reactions, especially to cases of general acid or base catalysis, or to hydrolyses where reactions involving both H_2O and OH^- contribute to the observed rate.

It can easily be seen that when the back reaction is of an order $\geqslant 2$, then the curve $\varphi(t)$ always starts out flat for low values of φ, growing gradually steeper and steeper, as exemplified in Figure 1. However since $\varphi \rightarrow 1$ as $t \rightarrow \infty$, such a curve must show a point of inflexion at a certain value of φ, and become concave towards the t-axis. Beyond this point, an expression of the type of equation IV cannot fit the experimental values*.

In the simple example

$$2A \rightleftharpoons 2X$$

this point of inflexion can be shown to occur when $\varphi = 1/3$, whereas in other simple cases rather complicated expressions are obtained, which contain the concentration of the reactants, and the equilibrium constant.

When the back reaction is of the order unity, the curve $\varphi(t)$ may in certain cases be concave towards the t-axis even at the lowest values of φ.

Our method should be considered empirical, and for every given case, the plot of the experimental values of φ against time should be inspected so that a suitable analytical expression for $\varphi(t)$ can be chosen.

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* When necessary, the continuation may be represented by a different power series containing negative coefficients, but even this combination will fit the experimental value of φ only over a limited range. When values of φ approaching unity are involved, the expression representing $\varphi(t)$ may well become so complicated that our method loses its advantage.

THE SYNTHESIS OF *dl*- AND *d*-PODOCARPAN-6-ONE, POTENTIAL INTERMEDIATES FOR THE SYNTHESIS OF DITERPENES*

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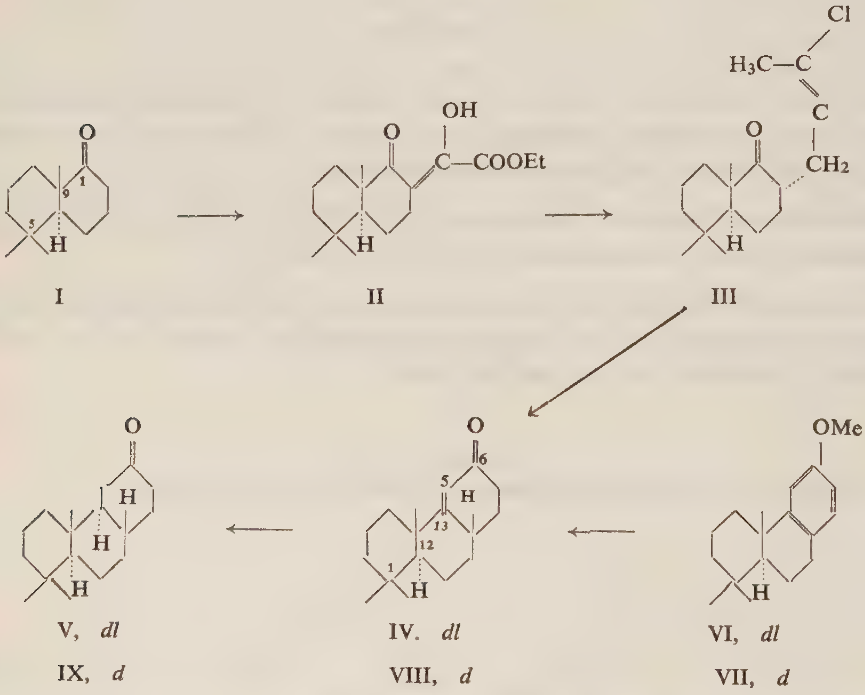
The Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth

We wish to report the synthesis of *dl*-podocarpan-6-one (V)*** and the corresponding *d*-compound (IX), potential intermediates for the synthesis of diterpenes of the rimuene and phyllocladene type.[1]



5,5,9-Trimethyl-*trans*-decal-1-one (I)[2] was transformed to the ethoxyoxalate (II) through condensation with diethyl oxalate by means of sodium hydride in benzene. Alkylation with 1-iodo-3-chlorobut-2-ene (from 1,3,-dichlorobut-2-ene and sodium

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* This is Part IX in the Series "Syntheses in the Terpene Series"; for Part VIII, see SONDHEIMER, F. AND WOLFE, S., 1959, *Can. J. Chem.*, **37**, 1870.

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*** The nomenclature and numbering is that proposed by KLYNE, W., 1953, *J. Chem. Soc.*, 3072.

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iodide) in boiling acetone in the presence of potassium carbonate and treatment of the non-acidic product with boiling ethanolic sodium ethoxide led to the chloroketone (III) [b.p. 140–160° (bath temp.)/1 mm.]. The action of 90% sulfuric acid on (III) at 0–20° for 16 hrs. produced *dl*-$\Delta^{5(13)}$-podocarpen-6-one. (IV) [b.p. 120–130° (bath temp.)/1 mm.; $\lambda_{\max.}^{\mathrm{EtOH}}$ 239 mμ, ε 13,300; semicarbazone: m.p. 206–207°; 2,4-dinitrophenylhydrazone: m.p. 171–173°]. The stereochemistry of the new asymmetric center of (III) and (IV) follows from the method of preparation. The method for converting (I) to (IV), a modification of the procedure of Prelog *et al.*,[3] was arrived at only after considerable experimentation and after it had been established that (IV) could not be obtained from (I) by reaction with methyl vinyl ketone.

Hydrogenation of (IV) in ethanol over palladium-charcoal stereospecifically yielded *dl*-podocarpan-6-one (V) (semicarbazone: m.p. 213–215°: 2,4-dinitrophenylhydrazone: m.p. 133–135°). α-Addition of hydrogen had been expected in view of the hindrance of the β-side of (IV) by the axial β-methyl groups attached to C-1 and C-12. The stereochemistry assigned to (V) was confirmed by the fact that the same substance was obtained from (IV) by reduction with lithium in ammonia and subsequent re-oxidation with chromium trioxide in acetic acid.[4]

For the synthesis of *d*-podocarpan-6-one (IX), the recently described optically active phenol methyl ether (VII) (from podocarpic acid)[5] appeared to be a suitable starting material. To determine optimum conditions, we worked first with the corresponding racemic ether (VI),[6] which on being subjected to Birch reduction with lithium in liquid ammonia-ethanol and then heated with hydrochloric acid in warm methanol produced the same unsaturated ketone (IV) as obtained by the first method. This reaction sequence was then applied to (VII), whereby *d*-$\Delta^{5(13)}$-podocarpen-6-one (VIII) [b.p. 90–100° (bath temp.)/0.1 mm.; $[\alpha]_D + 1°$ (chloroform); $\lambda_{\max.}^{\mathrm{EtOH}}$ 239 mμ, ε 13,500; semicarbazone: m.p. 230–231°] was obtained. Hydrogenation, as in the *dl*-series, then produced *d*-podocarpan-6-one (IX) [$[\alpha]_D$ + 28° (chlorofom); semicarbazone: m.p. 218–219°].

All the new substances described gave correct microanalytical results and the infrared spectra were in accord with the assigned structures.

We are indebted to Dr. R. Youssefyeh for carring out certain experiments and to Dr. B. Altman for technical assistance. Generous gifts of chemicals were made by Dr. I. R. McDonald (Dominion Laboratory, Wellington, New Zealand), Prof. R. A. Raphael (University of Glasgow, Scotland) and Prof. V. Prelog (E.T.H., Zurich, Switzerland).

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LETTERS TO THE EDITOR

The thermal decomposition of ammonium perchlorate in the presence of magnesium oxide.

A. HERMONI (MAKOVKY) AND A. SALMON, *Scientific Department, Ministry of Defence, Tel Aviv, and Technion—Israel Institute of Technology, Haifa.*

The thermal decomposition of ammonium perchlorate in the presence of magnesium oxide has been investigated in the temperature range 170–280°C. Between 170 and 230°C the decomposition reaction proceeded to completion. At higher temperatures, the decomposition was only partial, the percentage decomposed increasing with the temperature (Table I).

TABLE I

Percent of ammonium perchlorate decomposed in the presence of magnesium oxide at various temperatures

Temperature (°C)	*Percentage of ammonium perchlorate decomposed*
170–230	100
240	20
250	4.8
280	23

The final total pressure of nitrogen and oxygen obtained by the decomposition of 100 mg of ammonium perchlorate in the presence of 15 mg magnesium oxide varied with the reaction temperature (Table II).

TABLE II

Final total pressure of N_2+0_2 obtained at different temperatures from the decomposition of a mixture of ammonium perchlorate and magnesium oxide

Temperature (°C)	*Final pressure (mm.)*
225	1.5
240—290	10^{-2}
350	0.7
360	1.7
380	3.5
400	4.0

The rate of the decomposition of the mixture decreased, as the amount of the magnesium oxide increased (Fig. 1), and the ignition delay of powdered mixtures of the two compounds was higher than that of ammonium perchlorate alone.

A microscopic examination of a mixture of ammonium perchlorate with the oxide before and after partial decomposition showed that the particles of the oxide which had surrounded the salt before the reaction, had disappeared. At high temperatures the mixture melted. It is postulated that

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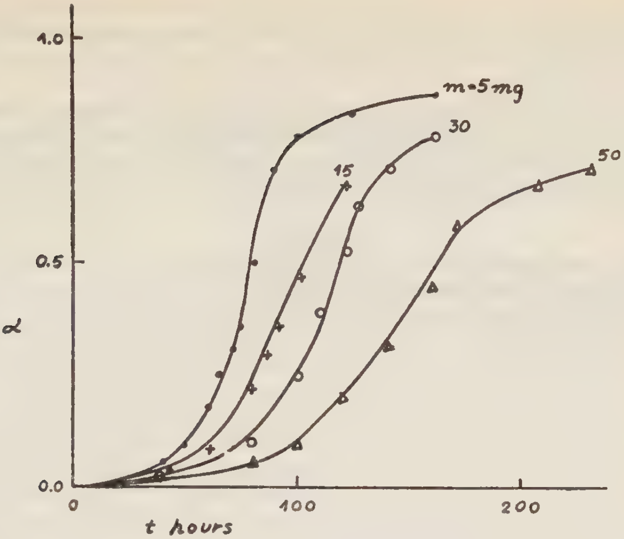

Figure 1
Rate of the decomposition of 100 mg of NH_4ClO_4 and m mg. of MgO at 180°C

under these conditions the magnesium oxide is converted to the corresponding perchlorate which forms a meltable eutectic with ammonium perchlorate.

Between 215—235°C the rate of decomposition of a mixture of 100 mg of ammonium perchlorate and 15 mg of magnesium oxide could be described by the contracting sphere formula

$$1-(1-\alpha)^{\frac{1}{3}} = K_1 t \qquad (1)$$

or by the Prout-Tompkins formula

$$\log \frac{\alpha}{1-\alpha} = k_2 t \qquad (2)$$

The Arrhenius parameters A_1, E_1, A_2 and E_2 calculated from the plot of $\log k_1$ and $\log k_2$ versus $1/T$ are given by:

$\log A_1 = 11.2 \pm 1.2$ $E_1 = 31.4 \pm 2.8$ Kcal
$\log A_2 = 10.8 \pm 1.3$ $E_2 = 29.2 \pm 3.0$ Kcal

The Pulse Technique in the isotope separation by Electromigration, MICHAEL M. BENARIE — *Israel Institute for Biological Research, Ness-Ziona*

A method for isotope separation by electromigration in aqueous solution has been reported previously[1]. In answer to a number of inquiries, a brief outline of the theory underlying the method will be given here.

In the electrolysis of solutions, by the use of very high field strengths ($>$10 kV/cm), the ionic velocities reach such high values that Stokes' law no longer applies with accuracy. For the highest field strengths, at which the velocities of the ions reach the order of one centimeter per second, the ion will move through many times the thickness of its atmosphere during the time of relaxation required to restore the spherically symmetrical distribution (Wien field effect[2,3]). Consequently, the velocities of each isotopic species appear separately, without the equalising hydratation effect, and the relative difference in migration velocity becomes comparable to that measured in the molten salt (but can not, of course exceed this value).

High field strength implies a correspondingly high current, and the ensuing boiling of the aqueous solution can be avoided only by applying short pulses of direct current. The frequency of the pulses is of no primary importance; it is determined by the total heat dissipation and the highest tension which is compatible with the isolation of the apparatus.

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BOOK REVIEWS

HETEROCYCLIC CHEMISTRY, AN INTRODUCTION, BY ADRIEN ALBERT, pp. 1–424, 1959, The Athlone Press. 45.*S*

The intention of this book is set out in the preface: "It aims to supply a sound framework to which each reader can attach new information as it comes his way".

Instead of dealing with the vast material in the conventional way according to ring numbers and kind and numbers of heteroatoms, the present book tries to correlate heterocyclic chemistry with the general, most familiar concepts of organic chemistry; it accordingly divides the subject into hetero-paraffinic, hetero-ethylenic, and hetero-aromatic substances. The latter, having the greatest individuality, are further subdivided on the basis of the π-electron content of the ring. Thus a separation of *π-deficient* N-heterocycles (allied to nitrobenzene in their chemical nature) from the *π-excessive* N-heterocycles (allied to aniline) is effected. This approach naturally leads to placing emphasis on principles rather than on isolated facts.

The author is of the opinion that this comparative method makes it possible for the beginner, after once understanding the plan of the book, to find his way through the vastness of heterocyclic chemistry by selecting additional reading in the book. In addition, the text is designed in such a way as to help more advanced readers also.

Generally, more emphasis is given to the connection between structure and properties than to syntheses, and parent substances are given more attention than their highly substituted derivatives. A prominent place is given to physical properties of the substances dealt with, e. g. in describing the use of infrared and ultraviolet spectra in problems of heterocyclic chemistry. On the other hand, considerations of reaction mechanism are omitted.

There may be a divergence of opinion as to whether the hopes of the author as regards the usefulness of this book for beginners will entirely materialise. But without question it will be most valuable for the student who is already somewhat familiar with the syntheses and reactions of heterocyclic chemistry, and who will find in this book means to organise his previous knowledge from new points of view.

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CHROMATOGRAPHIC REVIEWS, PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS, Volume I. Edited by MICHAEL LEDERER, Elsevier Publishing Company, 1959, Amsterdam - London - New York - Princeton.

The tremendous development of chromatography and its bearing on most branches of chemistry inspired the publication of this review series. The present volume contains the following nine chapters, dealing with the subjects indicated:

Chromatostrips and Chromatoplates (by E. Demole, Paris); High Voltage Electrophoresis (by H. Michl, Vienna); A Method for the Paper Chromatographic Separation and Identification of Phenol Derivatives, Mould Metabolites and Related Compounds of Biochemical Interest, Using a "Reference System" (by L. Reio, Stockholm and Lund); Methods for the Separation of South American Strychnos and Indian Curare Alkaloids (by G. B. Marini-Bettolo and G. C. Casinovi, Rome); Chromatography of Sterols, Steroids, and Related Compounds; an article previously published in book form in German in 1958 (by R. Neher Basel); Paper Chromatography of Chloroplast Pigments (by Z. Sestak, Prague); The Chromatographic Identification of Anthocyanin Pigments (by J. B. Harborne, Hertford); Paper Chromatography of Inorganic Phosphorus Compounds (by

H. Hettler, Heidelberg); and Separation of Isotopes by Chromatography and by Electrophoresis (by M. Chemla, Paris).

The articles are written by specialists in the respective fields and the treatment appears to be up-to-date throughout: Some of the contributions are excellent.

It is intended to publish annually an additional volume of this publication covering other selected topics in chromatography. There is no question that the publication under review constitutes a valuable, authoritative and handy source of information for chemists and biochemists who can rely on it for up-to-date information in the broad field dealt with.

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THE ENZYMES. Volume 1: Kinetics, Thermodynamics, Mechanism, Basic Propertties. Second edition, Eds.: Paul D. Boyer, Henry Lardy, and Karl Myrbaeck, Academic Press, Inc., Publishers, New York 3, N.Y., 1959, 785 pages with index, $24.00.

With the publication of this volume, the first of a new four-volume treatise, the publishers have embarked on an ambitious undertaking to "present fully the available information about enzymes and enzyme action on a molecular level". In order to make the price more "attractive", a fifteen percent reduction is offered to those who place an order for the complete set prior to publication of the last volume. The publishers consider the second edition supplemental to the original four volumes of "The Enzymes", and duplication of material is consequently held to a minimum.

The first volume is properly dedicated to the memory of the late Professor J. B. Summer who was, with Professor Myrbaeck, the co-editor of the first edition. It contains fourteen chapters, as follows: The Development of Enzyme Kinetics; Enzyme Kinetics; The Rate Equation For An Enzymic Reaction; Some Aspects Of The Thermodynamics And Mechanism Of Enzyme Catalysis; Structural And Stereospecificity; Enzyme Models; Mechanisms Of Transfer Enzymes; Coordination, Chelation, And Catalysis; Protein Structure And Enzyme Activity; Sulfhydryl And Disulfide Groups Of Enzymes; Other Reactive Groups Of Enzymes; Induced Formation Of Enzymes; and The Control Of Enzyme Activity.

In view of the extensive treatment given in each of these chapters, a detailed review of each chapter by a single reviewer would be nigh impossible. On reading the book, however, one is impressed with the excellent presentation of each subject matter. Of great interest is the first chapter which deals with the development of enzyme kinetics from a historical point of view. As such, it will serve the excellent purpose of acquainting the reader with many current ideas and concepts which are usually overlooked, because they are buried in old books on dusty library shelves. The student who may be induced to read this chapter, as well as some others, which rely heavily on historical development, will appreciate the genius and the high level of professional competence of three generations of teachers and scientists.

The editors have chosen competent and reputable investigators for each of the chapters, and consequently the quality of the book is above reproach. In reading the book, this reviewer has not found any serious errors. There occurs, however, some misrepresentation in the wording of the subtitle for volume one, according to which this volume should contain some articles on the basic properties of enzymes. One looks in vain for a chapter dealing with molecular weights, sizes, and shapes of enzymes, as could be expected from a volume dedicated to the presentation of enzymes on a "molecular level". Another notable ommission, which should have rated a chapter, is the treatment of the concept of hydrogen bonds in enzyme mechanisms. For instance, throughout the whole book there are a total of only fourteen short references to hydrogen bonds.

Two chapters, namely the one on Enzyme Kinetics and the one on Coordination, Chelation, and Catalysis, are very advanced, though sometimes speculative. In view of this, one would logically expect the inclusion of a chapter dealing with newly developed techniques in enzyme studies which have just emerged as possible tools. For instance, a discussion of nuclear magnetic resonance, or solution infrared spectroscopy, or rotatory dispersion, to cite just a few, would have been helpful. Certainly, the theories underlying such very recent developments and techniques could have given some readers new ideas and might have planted fruitful seeds in some investigators' minds. If a book can accomplish such stimulation, it would more than offset the high price. It is hoped that the editors have in mind such possibilities for some future volume, but their intentions in this respect are not clear from the advertised contents of the volumes to follow.

On the whole, this reviewer feels that the published volume represents another mark of achievement in scientific publications. There is no question that this book is excellent and brings the reader up to the year 1958. No book of this nature can be perfect, nor can it fit needs of all interested persons. It is hoped that it will enjoy a wide circulation, and that the publishers will even find a way to give students special discounts, in order to furnish them with a badly needed, valuable reference handbook.

ERIC ELLENBOGEN*
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DIE BLUTEIWEISSKORPER IN DER ULTRAZENTRIFUGE SEDIMENTATION - FLOTATION by Dr. K. JAHNKE und Dr. W. SCHOLTAN, Georg Thieme Verlag, Stuttgart 1960. 207 p. 72 figures, 63 tables, DM 49.50.

Three factors were the main cause in bringing clinicians, besides biochemists and physiologists, into close contact with the method and theory of the separation of plasma proteins by the ultracentrifuge: (1) The most important factor was the introduction of the flotation method by I. W. Gofman and his co-workers and the finding that it is probably a connection between the amount and ratio of lipoproteins in the serum and the development of coronary sclerosis; (2) The discovery of an as yet unknown disease — the macroglobulinemia — by Waldenstroem; (3) The construction of new and simpler models of ultracentrifuges that could give reliable results. In spite of this latter fact it seems unlikely that this method will be adopted on a wide scale in hospitals and laboratories in the near future. Nevertheless, already now, many clinicians are clamoring for orientation in this method in its theoretical and practical aspects. Only very recently there appeared an excellent monograph by H.K. Schachman on the ultracentrifuge, that dealt with the problems of the sedimentation technique from a more physico-chemical standpoint. This book will therefore be a very valuable addition especially for doctors and biologists. Along with the description of the principles of sedimentation analysis and the equipment in general use today, the reader will also get a theoretical basis of the sedimentation of the proteins, and the methods by which the results could be utilized.

The authors speak about normal serum and serum of different diseases. A special chapter, deals with the paraproteinemic syndromes (macroglobulinemias and plasmacytoma globulines) another chapter with different dysproteinemic syndromes. The largest chapter is dedicated to the flotation of the lipoproteins and the reader can learn through it the entire technique and the physical and chemical properties of the lipoproteins, the normal lipoprotein spectrum of the serum and especially the pathological lipoprotein spectrum in atherosclerosis and other diseases more or less connected with atherosclerosis.

The authors, one an experienced doctor, the other a physico-chemist of high standing, have succeeded in producing a good and complete review containing the relative literature in this field. The interested clinician will no doubt obtain his theoretical, methodical and clinical orientation in this field.

E. WERTHEIMER, M. D., Jerusaləm.

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* Deceased

THE XXVIIth SCIENTIFIC MEETING
ISRAEL CHEMICAL SOCIETY

Rehovoth, October 10—11, 1960

Physical Chemistry

First Session, October 10, 1960 Chairman: E. FISCHER

Intramolecular energy transfer

O. SCHNEPP, M. LEVY AND Z. SILBERMAN, *Department of Chemistry, Technion — Israel Institute of Technology, Haifa*

Intramolecular energy transfer has been demonstrated in three homologous 9-anthryl-1′-naphthyl-alkanes in which the anthracene and naphthalene units were joined by saturated chains of one, two and three carbon atoms[1]. The absorption spectra of these compounds demonstrate that the π- electron systems of the two aromatic units do not interact appreciably. In the present work, the naphthalene group was excited by appropriately filtered radiation while the observed fluorescence was characteristic of the anthracene group. From the analysis of comparative fluorescence intensity measurements, relative as well as absolute values of the quantum yields of the intramolecular energy transfer are obtained. These results are of value as they can be used to verify the theory of sensitized fluorescence due to Foerster[2].

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The influence of polyelectrolytes on the absorption spectra of acridine orange

G. BLAUER, *Brandeis University, Waltham, Mass., U.S.A.*

Spectral changes caused by interaction of acridine orange with negatively charged macromolecules at various degrees of ionization are reported and discussed.

Flash – excitation of acridine orange in solution

G. BLAUER AND H. LINSCHITZ *Brandeis University, Waltham, Mass., U.S.A.*

The absorption spectrum of the metastable state of acridine orange, its decay kinetics and chemical interactions are reported.

Oscillator strengths of the absorption bands of halide ions in solution

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The nature of the charge distribution in the excited state of halide ions in solution was investigated by the calculation of the intensities of their UV absorption bands. Slater type one-electron wave functions were used to represent the orbitals of the p electrons in the ground state. Two alternative pictures were adopted for the description of the excited state:

a) The electron in the box model[1]. The wave function of the excited state was chosen as the ground state wave function for a particle in a spherical box.

b) The hydrogen-like model [2,3] was characterized by a nodeless 2s Slater wave function with an effective charge Zef = 1/Dop — 1/Ds.

The comparison of the experimental and theoretical results for Cl^- Br^- and I^- indicates that fair agreement is obtained by application of the hydrogen-like model. The gradual increase of the oscillator strength with increasing ionic radius is satisfactorily accounted for.

These results yield additional support to the validity of the physical picture of electron binding in solutions in the field of a polarized dielectric medium.

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The absorption intensity of $X{=}O^{18}$ groups stretching bands

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According to the view commonly accepted at present an isotopic exchange does not appreciably affect such physical properties of a compound which are not directly connected with the mass of its constituent atoms; hence it can be expected that the absorption of $X{=}O^{18}$ stretching bands (X=C, P) will be only slightly different from that of corresponding $X{=}O^{16}$ bands. It was however observed that this is not the case: benzophenone [1], triphenylphosphine oxide [2], benzamide, monomeric benzoic acid, methyl benzoate and methyl benzamide all show molecular extinction coefficients and relative integrated absorption intensities which are 10-20% different in the case of the $X{=}O^{18}$ bands relative to their values in the corresponding $X{=}O^{16}$ bands. Usually the labelled groups show the lower absorption, but in benzamides (in CCl_4) the $C{=}O^{18}$ band is stronger than the $C{=}O^{16}$ band.

The influence of changing the solvent, from CCl_4 to $CHCl_3$, on the X=O frequency (and the benzamide NH_2 frequencies), the intensity of the ultraviolet $n \rightarrow \pi^* C{=}O$ bands [3], the electrical moment of benzophenone [3], the CCl_4 solvation effect on the $X{=}O$ band-width [2], the force constant of other bonds in $X{=}O$ molecules etc. were all found to be materially different in $X{=}O^{18}$ molecules from their values in the corresponding $X{=}O^{16}$ analogues. All these phenomena are explicable by assuming that for some reason as yet unknown the polarization of $X{=}O$ π electrons is different in $X{=}O^{18}$, giving higher electrical charges on the O^{18} but lower $\partial e/\partial r$.

The spectrum of adsorbed benzene

A. Ron, M. Folman and O. Schnepp, *Department of Chemistry, Technion—Israel Institute of Technology, Haifa*

Benzene was adsorbed on porous Vycor glass and its electronic absorption spectrum in the 2600A region was investigated at liquid nitrogen and liquid hydrogen temperatures. The spectral lines were considerably sharpened by sintering the glass at 950°C before adsorption. In addition to the spectrum of the free molecule, the forbidden pure electronic transition due to the perturbation of the surface is observed to appear. Fine structure is observed and is interpreted as being characteristic of a vibrational degree of freedom of the adsorbed molecule with respect to the surface. In the electronic ground state the observed spacing is 120 ± 20 cm^{-1}.

Physical Chemistry

Second Session Chairman: F. S. Klein

An approximate treatment of the kinetics of parallel reversible reactions

Assa Lifshitz and B. Perlmutter-Hayman, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

When we have a reaction scheme of the type

$$A + B \rightleftharpoons B' + X + Y + \ldots.$$

$$A + C \rightleftharpoons C' + X + Y \ldots.$$

where B, C, B′ and C′ are in rapid equilibrium with each other, the two reactions often cannot be studied separately. In such cases, the rate constants have to be evaluated by some trial and error method. However, integration of the rate equation may yield an unwieldy expression which is not very suitable for that purpose.

The rate equation can be written in the form :
$dx/dt =$ (rate of forward reaction) $[1 - \varphi(x)]$
where x is the amount of product present at time t, and $\varphi(x)$ is the ratio of the total

rate of the back reaction to that of the forward reaction. Provided the appropriate equilibrium constants are known, $\varphi(x)$ can be evaluated for every given value of x, where x in turn is of course a function of time. Now, it was found that when this $\varphi(x)$ was plotted against the correponding values of time, a simple curve is often obtained which can be conveniently represented as a short power series in time, $\varphi(t)$.

The rate equation can then be transformed into the approximate form:

$$\frac{dx}{\text{rate of forward reaction}} = [(1 - \varphi(t)]\, dt$$

After integration, this yields a much simpler expression than that obtained by integration the exact form.

The method, which is applicable to many catalytic reactions in solution, is demonstrated for the hydrolysis of chlorine in the presence of acetate.

The hydrogen evolved from evacuated water solutions of ethanol irradiated with X-rays

CHAVA LIFSHITZ AND GABRIEL STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

Ionizing radiations form in water H and OH radicals. The H atoms are able to abstract hydrogen atoms from dissolved ethanol and yield molecular hydrogen [1]. The nature of this reaction was investigated. By means of isotopic labelling of the water and/or the ethanol it was found that the preference of attack on the hydrogen of the ethanol is in the order: $\alpha > \beta >$OH.

The possibility exists for basic [2] and acidic [3] forms of H atoms. The exact nature of the attacking species reacting with the ethanol is unknown. The *p*H dependence of the D content of the evolved gas from $CH_3\ CD_2OH$ in H_2O was investigated. This was fiund to be in accord with the *p*H dependence found for the system $D_2 — H_2O$[4] and is explained by:

(a) the abstraction reaction occurring according to:

$$CH_3\ CH_2\ OH + H \longrightarrow H_2 + CH_3\ CHOH$$

(b) the *p*H dependence of the ratio e(aq)/H

(c) the possibility of the formation of H_2^+ below $pH = 3$.

This research was sponsored by the Israel Atomic Energy Commission.

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Molecular and atomic isotope effects in radiation chemistry of water solutions

CHAVA LIFSHITZ AND GABRIEL STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The primary act brought about in water solutions by ionizing radiations gives molecular hydrogen, the yield of which is lowered only by high concentrations of radical scavengers, as well as atomic hydrogen, which may give molecular hydrogen with suitable scavengers (e.g. Fe^{++} (H^+), ROH).

Isotope effects produced in the hydrogen formed when H_2O — D_2O mixtures are irradiated were investigated in order to elucidate the machanism of the primary act as well as of secondary reactions.[1, 2, 3]

This was further taken up by us. We investigated the dependence of isotope effects on *p*H, type of solute, solute concentration and deuterium concentration. Denoting α_M as the isotope effect for molecular formation of hydrogen, and α_A as the isotope effect for hydrogen formed via H atoms, α_M in acid solutions containing 1% D was found to equal 2 and to be independent of the type of solute. α_A was found to equal 4 in similar solutions, being likewise independent of the solute.

At neutral *p*H both α_M and α_A are lower. This points to the possibility of a similar initial mechanism of formation. It was found that α_M depends upon the deuterium concentration of the solution while α_A does not. The dependence is such that a bimolecular mechanism is suggested for the formation of the molecular product.

α_M was found to be independent of the concentration of the radical scavenger within a range of concentrations. This shows that no change of mechanism is involved. The influence of concentration changes was especially investigated in acid iodide solutions. Such concentrated I^- solutions give further production of hydrogen, besides the molecular product but the α for the total gas does not change significantly with iodide concentration. It seems that the mechanism of reaction of H atoms with Fe^{++} ions and I^- ions in acid solutions are different.

This research was sponsored by the Israel Atomic Energy Commission.

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The action of X-rays on aqueous solutions of ferro-ferricyanide and the influence of added solutes

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Dilute aqueous solutions of ferri and ferrocyanide were irradiated in the absence and in the presence of added solutes.

We confirmed the reaction mechanism and computed relative rate constants of ferrocyanide, glycine, alanine, ethanol and formate with OH radicals.

The stability of ferri-ferrocyanide in a wide range of *p*H values enabled us to investigate the influence of *p*H on these rate constants.

A relation was found between the rate constant for the reaction of the amino acids with OH and the *p*K of the amino acid.. Amino acids with a neutral amino group are very reactive towards OH radicals as compared to the zwitterion,

The results may clarify the situation with complicated oxidation reduction systems such as cytochrome c. In this case differences in the reduction yields of cytochrome had been found when various solutes had been present [1]. We also found a *p*H dependence of the reduction yield of cytochrome c when amino acids were added which fits the results with ferro-ferricyanide.

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Isotopic exchange of hydrogen with liquid ammonia

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The isotopic hydrogen exchange between molecular hydrogen and liquid ammonia is strongly catalysed by sodamide or potassamide. In the present work this reaction was studied under various experimental conditions.

In preliminary experiments it has been verified that the reaction studied is not diffusion controlled, i.e. it is independent of the rate of mixing. For this purpose sodamite was used as catalyst, since because of its small solubility a saturated solution could be prepared and the constancy of the catalyst concentration could be assured. A method of estimating the solubility of hydrogen in liquid ammonia was developed. The solubility is 0.06 cc $\frac{\text{NTP}}{\text{g}\cdot\text{atm}}$ at –40°C. A knowledge of this quantity is essential in order to calculate the absolute rate of the exchange reaction. An activation energy of 10 Kcal/mol in the temperature range of –35°C to –65°C was found from an Arrhenius plot of the reaction rates. This activation energy is equal for the two catalysts mentioned and is also equal, within experimental error, for both HD and D_2 molecules. The ratio of the exchange rates for D_2 and HD respectively was found from direct measurements and by graphical methods. Its value is 1.65 ± 0.05. Experiments with the more soluble potassamide made it possible to study the dependence of the reaction rates on the catalyst concentration. The exchange was found to be proportional to the square root of the catalyst concentration.

Physical Chemistry

Third Session, October 10, 1960 Chairman: B. Perlmutter-Hayman

The hydrolysis of fluoborates

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The hydrolysis reaction of BF_4^- to boric acid and fluoride ions in the pH range 4–14 was investigated and was found to be zero order in OH^- $R = k[BF_4^-]$ which implies a typical S_N1 reaction, the rate determining step being the dissociation reaction $BF_4^- \rightarrow BF_3 + F$, followed by a fast hydrolysis of BF_3. In the acid region the hydrolysis is found to be acid catalysed, $R = K_a[H^+][BF_4^-]$. There is no catalytic effect of HF or HSO_4^- which implies a specific acid catalysis with a pre-equilibrium $H^+ + BF_4^- \xrightarrow{\text{fast}} HBF_4 \xrightarrow{k} BF_3 + HF \xrightarrow{\text{fast}} HBF_3OH + HF$. It was found that addition of a proton to the BF_4^- ion does not reduce the activation energy of the cleavage of the B–F bond, but spectacularly increases the entropy of activation. These results corroborate former work on the formation of fluoborates [1] and on the isotopic exchange between hydrofluoric acid and fluoborates [2].

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The chloramine ammonia reaction in water

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The mechanism of the reaction between chloramine and ammonia, the Raschig synthesis of hydrazine, has recently been subject to extensive discussion [1], [2], [3].

Both the rate of disappearance of NH_2Cl and the rate of formation of N_2H_4 have been followed. The yields of hydrazine varied between 55% and 80%, depending on conditions. The experimental results show that the rate of the reaction

$$NH_2Cl + NH_3 + OH^- \longrightarrow N_2H_4 + Cl^- + H_2O$$

is first order with respect to NH_2Cl and first order with respect to NH_3. When the OH^- concentration is below 0.1M the rate is independent of OH^- concentration. At higher alkalinities a second order reaction in OH^- predominates. At 27°C the overall rate is given by the expression:

$$\frac{d(NH_2Cl)}{dt} = k_1\,(NH_3)\,(NH_2Cl) + k_2(OH^-)^2(NH_3)(NH_2Cl)$$

$k_1 = 6{,}7 \times 10^{-3}\ \mathrm{l.mol^{-1}min^{-1}}$
$k_2 = 6{,}0 \times 10^{-3}\ \mathrm{l^3mol^{-3}min^{-1}}$

The implications of these results were discussed.

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The mechanism of the hydrolysis of chlorine

Assa Lifshitz and B. perlmutter-Hayman, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The mechanism of the hydrolysis of chlorine in pure water, as proposed by Shilov and Solodushenkov [1]:

$$(1)\ Cl_2 + H_2O \xrightarrow{k_{H_2O}} Cl^- + H^+ + HClO$$

has been verified in a series of experiments using a continuous flow apparatus [2]. It was also shown that the contribution to the rate of hydrolysis of the parallel reaction

$$(2)\ Cl_2 + OH^- \xrightarrow{k_{OH^-}} Cl^- + HClO$$

is negligible because of the very slow production of hydroxyl ions from the self-dissociation of pure water [3].

In the presence of acetate ions, where the hydrolysis is given stoichiometrically by the equation

$$(3)\ Cl_2 + H_2O + Ac^- \xrightarrow{k_{Ac^-}} Cl^- + HAc + HClO,$$

the rate of reaction was found to be much higher. On the other hand, in the presence of $NaClO_4$ the rate was about the same as that in pure water. This shows that acetate ions do not act as an "inert salt".

In a series of experiments in which the concentrations of acetic acid and acetate ions were changed, it was found that the accelerating effect of the acetate ions is caused by two additional parallel reactions, namely reactions (2) and (3).

In contradistinction to the situation in pure water, in the presence of acetate ions the hydroxyl ions are supplied by a faster mechanism [4], viz.,

$$(4)\ Ac^- + H_2O \longrightarrow OH^- + HAc,$$

and their concentration is calculated from the two consecutive reactions (4) and (2), using the steady-state hypothesis.

By making suitable extrapolations the value of k_{Ac^-} and the order of magnitude of k_{OH^-} were found. The latter shows that reaction (2) is diffusion-controlled.

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Hydrolytic degradation of tri n-butyl phosphate in the presence of hydrochloric acid and uranyl chloride

M. HALPERN AND A. S. KERTES, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

The acidolytic degration of tributyl phosphate at varying concentrations of hydrochloric acid and uranyl chloride has been followed using physical-chemical methods of analysis. The rate of hydrolysis, which is first order with respect to the ester, was compared with that of a similar system containing nitric acid amnd uranyl nitrate.

The products of hydrolysis with uranium (IV), formed in the system by photo-sensitized reduction of uranium (VI), resulted in an unextractable compound, in marked contrast to a similar system containing the nitrates.

The isotopic exchange of oxygen between hydrogen peroxide and water catalysed by nitric acid

M. ANBAR AND S. GUTTMANN, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth*

The oxygen exchange between hydrogen peroxide and water was studied using highly enriched H_2O^{18}. No exchange was detectable in neutral solutions ($k < 5.10^{-8}$ $min^{-}1$) under the most sensitive conditions. In the alkaline range 1N OH^- an extremely slow exchange could be followed ($k < 1{,}2.10^{-7}$ min^{-1} at 25°C). In the acid range using 4N perchloric acid no appreciable exchange was measurable ($k < 5 \times 10^{-8}$ $min^{-}1$ at 60°C). At the same acid concentration in sulphuric acid, a rather faster exchange was observed ($k = 1{,}2.10^{-7} min^{-1}$ at 60°C), and at 7M H_2SO_4 the rate increased by a factor of ten. Nitric acid catalysed considerably the H_2O_2 – H_2O exchange $k = 1.7\ 10^{-5} min^{-1}$ in 4M HNO_3 and $k = 2.66\ 10^{-4} min^{-1}$ in 7M HNO_3 at 60°C. This catalysis may be due to the formation of the hydroperoxides O_3SOOH and O_2NOOH in equilibrium with H_2O_2 which may undergo exchange with the solvent. The inductive effect to the acid group O_2N– or O_3S– may polarize the O-O bond and make it vulnerable to an attack by water, The findings may be related to former results on induced isotopic exchange of H_2O_2 with water on interaction with various oxidants and reductants.

Chloride ion catalysis of the isotopic exchange between nitrate ions and water

M. ANBAR AND S. GUTTMANN, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth*

The isotopic exchange of oxygen between HNO_3 and H_2O has been extensively studied [1]. It has been established that NO_2^+ or its hydrated form $H_2NO_3^+$ are responsible for the exchange process. Next it was found that nitrite ions enhance the exchange [2] and this has been attributed to an equilibrium involving N_2O_4. We have found that chloride ions catalyse the exchange reaction according to the rate law $R = k\ [H^+]\ [Cl^-]\ [HNO_3]$. This result may imply that the rate determining step is the nucleophilic attack of Cl^- on the $H_2NO_3^+$ with a displacement of water forming NO_2Cl, which undergoes fast hydrolysis to Cl^- and $H_2NO_3^+$. A similar behaviour was observed studying the effect of Cl^- on the isotopic exchange between bromate ions and water [3]. It seems probable that the rate determining step in the isotopic exchange between oxy anions and water, which involves the conjugated acid $H_2XO_n^+$, is a nucleophilic attack on this species, and the nucleophilic reagents may include water as well. These results may find further analogy in the second order term in the rate expression of the exchange between nitrous acid and water in absence of buffers[4] $R = k\ [NO_2^-]\ [H^+]\ [HNO_2]$ and the effect of buffers including phosphate [5] and acetate [6] on this reaction.

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Electrolysis of hydrogen peroxide (H_2O_2 ^{16,16}) in highly enriched H_2O^{18}

M. ANBAR, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth*

H_2O_2 ^{16,16} solutions (0.2M) in H_2O^{18} (92% O^{18}) have been electrolysed with Pt electrodes (C.D. — 2 Amp/cm^2) at various pH values (0.2 — 11.3); both the gas and the residual H_2O_2 were analysed for their isotopic composition. Any H_2O_2 formed from the water under these conditions would be protected by the excess of H_2O_2 in solution. It was found that H_2O_2 decomposes at a electrochemical yield of 1 mol/2 Faradays and H_2O_2 ^{18,18} was formed at a yield of 0.025 mol/Faraday. No formation of H_2O_2 ^{16,18} or of O_2 ^{16,18} could be detected under any circumstances.

When the electrolysis was carried out in an electrolyser with a sintered glass membrane so that no oxygen could reach the cathode, no H_2O_2 ^{18,18} was formed at all.

The results imply :

1. That no free OH radicals from water are involved in the anodic oxidation of water or of H_2O_2, as was suggested[1]; this would lead to a partial isotopic exchange with H_2O_2 ^{16,16} [2]. The oxidation of H_2O_2 probably occurs via platinum oxide ($PtO + H_2O_2 \rightarrow H_2O + O_2$) whose formation during anodic oxidation of water was suggested.
2. That no free HO_2 radicals are formed by *one*-electron transfer process (HO_2+ HO_2) as this radical would form OH radicals by $HO_2 + H_2O_2\ OH + H_2O + O_2$ and these would cause isotopic scrambling.
3. H_2O_2 ^{18,18} from the water is formed only by reduction of molecular oxygen on the cathode either by H atoms or by a double electron transfer. No H_2O_2 is formed by OH radical combination on the anode. This result confirms the assumption that the anodic oxidation of water involves labile oxides of the electrode rather than OH radicals formed by electron transfer [2].

Thus a double electron transfer mechanism seems more probable both for electrochemical formation and decomposition of hydrogen peroxide.

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Physical Chemistry

Fourth Session, October 11,1960 Chairman: M. Halmann

The hydrolysis of carbamoyl-phosphate

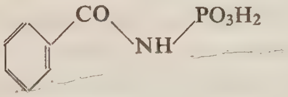
M. Halmann, Aviva Lapidot and David Samuel, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth*

The solvolysis of carbamoyl phosphate $NH^2{-}CO{-}O{-}PO_3H_2$ was studied in aqueous solution. The rate is proportional to the stoichiometric acid concentration below *p*H 4.0, is independant of acidity or added ions in the *p*H range 2 to 6, and is very slow in basic solution. The rate is faster in H_2O than in D_2O at *p*H 4, and oxygen 18 tracer studies indicate that both P-O and C-O bond fissions occur throughout the acid range. The mechanism of solvolysis of carbamoyl-phosphate will be discussed and related to its many functions.

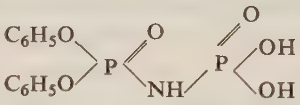
The solvolysis of N-acylphosphoramidic acids

M. HALMANN, AVIVA LAPIDOT AND DAVID SAMUEL, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth*

The hydrolysis of N-benzoyl phosphoramidic acid (I) and of 0,0′–diphenyl imidodephosphoric acid (II) were investigated by means of kinetic and isotopic techniques.



(I)



(II)

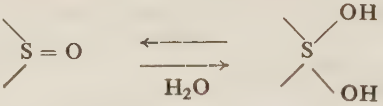
The rate of hydrolysis of (I) showed a maximum at pH = 4.0 and an isotope effect on solvolysis in D_2O. Compound (II) is hydrolysed at a slower rate, and also showed a rate maximum at $p\mathrm{H}_4$ but no isotope effect. The mechanism of solvolysis of these compounds is apparently sensitive to substitution on nitrogen which affects the rate and extent of protonation. The mechanisms of hydrolysis will be discussed.

The properties of the sulphur-oxygen bond

DAVID SAMUEL AND MARTA WEISS-BRODAY, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth*

The isotopic exchange of oxygen with diphenyl sulphoxide, diphenyl sulphone and diethyl sulphate has been investigated in acid and basic solutions.

No evidence for the reversible formation of a tetracovalent intermediate of the type (I) as suggested by Kursanov and Kudyavstev [1]



was found. These and other reactions of these compounds will be discussed.

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The oxidation of cotton by hypochlorite — A kinetic study*

J. A. EPSTEIN AND M. LEWIN, *Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

The rate of oxidation of cotton by hypochlorite solutions of concentrations 2 to

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* This work forms part of the research being carried out at the Institute under grant No. FG-Is-101-58 issued by the Agricultural Research Service, U.S. Dept. of Agriculture.

4×10^{-2} equ/l. was studied at *p*H values from 5 to 10. The reaction was followed either by periodic removal of small aliquots which were titrated iodometrically, or by automatically recording the alkali consumed to keep the *p*H constant, after it was established that the alkali consumed is equivalent to the hypochlorite decomposed.

The variation of the rate of oxidation with *p*H is generally similar to that obtained by Clibbens and Ridge [1] and by Rutherford et al. [2], having a comparatively flat maximum at a *p*H of about 7 and falling off rapidly as the *p*H is lowered or increased. Similar variations in rates were obtained in the oxidation of methyl glucoside [3] and alginic acid [4] with hypochlorite, and in the conversion of hypochlorite to chlorate[4]. It seems therefore that the rate is controlled by the composition of the hypochlorite solution which varies with the *p*H and not by the properties of the substrate.

The experimental results agree with the following empirical equation:

$$\text{Rate} = k\ [\text{HOCl}]^2 .\ [\text{OCl}'-]^{\frac{1}{2}} .$$

A tentative interpretation of the mechanism of the reaction is offered.

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Some Kinetic aspects of mild oxidation of wheat starch by sodium hypochlorite in alkaline *p*H range

J. Schmorak, D. Meizler and M. Lewin, *Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

Some kinetic aspects of mild oxidation of wheat starch by sodium hypochlorite in the *p*H range 7.5-11.0 were studied. No significant chlorate formation was observed at any time. From this and from other experimental evidence it is concluded that the reaction is most likely to be purely chemical in type and to proceed according to the scheme

$$\text{Starch} + \text{NaOCl} = \text{Starch. O} + \text{NaCl}$$

The reaction appears to be of the first order with respect to starch. It appears to be of the first order with respect to hypochlorite at *p*H=8. At pH 9 and 10 the reaction velocity is still approximately proportional to the concentration of the oxidant remaining in the solution, but its course appears to be more complicated. Its rate

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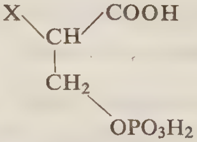
** This work forms part of the research being carried out at the Institute under grant number FG-Is-102-58 issued by the Agricultural Research Service, U.S. Dept. of Agriculture.

decreases with increasing pH of the oxidising medium. An approximate empirical equation is proposed, adequately representing the interdependence of the first order constant and pH in the pH range 7.5-10. The activation energy of the reaction is within the range of 21-23 Kcal/mole, i.e. that obtained very often for homogeneous, true chemical reactions. When the granular structure was destroyed, the rate of reaction increased by about 50%, and hence it may be deduced that the reactive sites available for hypochlorite oxidation when the starch is in its granular form are about two thirds of those available in solution. This points to a surprisingly loose structure of the starch granule. The addition of neutral salts had an accelerating effect on the reaction rate. Under the conditions employed this effect was negligible, but whenever larger amounts of neutral salts are present or formed in the course of the reaction the effect would have to be taken into consideration.

The solvolysis of serine-phosphate and related compounds

David Samuel and Brian Silver, *Department of Isotope Research, The Weizmann Institute of Science, Rehovoth.*

The solvolysis of serine-phosphate (I) in alkaline and acid solution and in the presence of enzymes has been examined, using kinetic and isotopic techniques. The alkaline solvolysis of these compounds appears to proceed by an elimination mechanism involving loss of a proton and fission of the C-O bond. This mechanism has not previously been found for simple phosphates. The mechanism of solvolysis of β-hydroxy propionici (II) and glyceric acid -O - phosphates (III) have also been investigated and related to the reactions of naturally occurring phosphoric acid derivatives.



I $X = NH_2$

II $X = H$

III $X = OH$

Physical Chemistry

Fifth Session, October 11, 1960 Chairman: M. Lewin

Polymerization of nitroethylene in dimethylformamide amd tetrahydrofurane

J. Grodzinski, A. Katchalsky and D. Vofsi, *Department of Polymer Research, The Weizmann Institute of Science, Rehovoth*

The polymerization of nitroethylene in dimethylformamide and tetrahydrofurane was studied over a wide temperature range, using pyridine and 3-methyl-4-ethylpyridine as catalysts*.

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* This work is in partial fulfilment of J. Grodzinski's Ph. D. thesis at the Hebrew University of Jerusalem.

Two distinct reaction mechanisms seem to be operating, depending on the temperature range.

At low temperatures (—75°C to —105°C) the kinetics are first order with respect to catalyst and monomer in both solvents. The degree of polymerization is proportional to the degree of conversion divided by the initial catalyst concentration. High molecular weight polymers are formed having specific viscosities of the order of 2. The overall activation energy is close to zero.

In the higher temperature range (25°C) the kinetics are second order with respect to monomer amd first order in catalyst concentration. The apparent activation energy is negative, and lower molecular weight polymers are isolated.

It is suggested that at low temperatures initiation proceeds by complex formation between catalyst and monomer, resulting in a dipolar active species. Propagation takes place by addition of monomer to the negative pole, the positive pole forming the "gegen-species". Pole separation in these solvents at low temperatures is maintained throughout polymer growth and no termination takes place. The formation of a "living polymer" is postulated.

As the temperature increases, termination of chain growth becomes more probable, causing the above mentioned change in reaction kinetics.

When isolated from the polymerization mixture, the polymers are of low stability, the specific viscosity falling off with time. However, on continued treatment with acids the polymers are stabilized.

The degradation of the poly-nitroethylene at temperatures between 60°C and 120°C was also studied. The main product of the degradation is water. This, together with spectroscopie evidence suggests that an internal oxidation-reduction is taking place.

The influence of saturated hydrocarbons on the rate of polymerization of olefines

Pinchas Jawetz, Chia Eden and Hans Feilchenfeld, *Petrochemical Laboratory Department of Physical Chemistry, The Hebrew University of Jerusalem and Nationa Council for Research and Development*

It has been shown [1] that the polymerization of ethylene by Ziegler catalysts follows a first order law with respect to olefine. Recently it has been observed [2] that the rate also depends on the partial pressure of ethane present

This surprising phenomenon was investigated and it was found that in the polymerization of both ethylene and propylene, ethane and propane retarded the reaction beyond a mere dilution effect.

Two explanations are possible: The rate constant of polymerization of the olefine is greater than (or of the same order as) that of adsorption. Alternatively a layer of saturated hydrocarbon may have built up around the catalyst which inhibits the diffusion of the olefine onto the catalyst surface. In both cases the concentration of the olefine on the catalyst is thus less than what would be expected from its partial pressure in the bulk of the gas. It is shown that this is not in contradiction with the assumption commonly made for first order heterogenous reactions, that only a small fraction of the active catalyst sites is covered by the reactant.

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On an electric field effect in polymerization and some of its consequences

Nehemia Shavit, *The Weizmann Institute of Science, Rehovoth*

It is shown that a chemical reaction involving molecules with electric dipole moment may be affected by the application of an electric field. The electric field imposes anisotropic conditions on the reaction system and may be expected to influence rates and alter types and properties of the products.

Electric fields may arise on the molecular level from ions and polyions or from dispersed colloidal charged particles or from an externally applied electric potential.

The polymerization in an external electric field of monomers having dipole moment and some of the properties of the polymers obtained, including the electric polarization (*electret* effect), are discussed.

Homogeneous polyacid-polybase fibers

I. Michaeli, M. Jeselson, A. Katzir, *Polymer Department, The Weizmann Institute of Science, Rehovoth*

A study of the preparation and properties of a new type of fibers containing mixtures of polymethacrylic acid with either polyvinylpyridine or polyvinylpiperidine is reported.

Both the drawing-off mixture and the final fibers are shown to be affected by the polyacid-polybase interaction.

The study of the solubility of the fibers in aqueous solutions shows three different *p*H ranges:

a. Complete solubility.
b. Full insolubility.
c. Extraction of one of the components following its dissolution.

A discussion of this behavior is presented in terms of polyelectrolyte interactions.

Physical Chemistry

Sixth Session, October 11, 1960 Chairman : U. GARBATSKI

The influence of surface conditions on the expansion of a solid due to the adsorption of non-polar gases

Y. KOZIROVSKI AND M. FOLMAN, *Department of Chemistry, Technion — Israel Institute of Technology, Haifa*

It is known that a solid adsorbent expands on adsorption of gases due to a lowering of its surface tension[1]. The extent of this expansion may be related to the elastic properties of the solid provided the lowering of surface tension is known. This value may be calculated from the modified Gibbs's equation on the assumption that it is equal to the spreading pressure of the adsorbed gas.

Previous work[2] showed that surface conditions influence to a large extent the expansion characteristic in case of adsorption of polar gases.

In this work the influence of the exchange of $^{-}$OH groups present on the surface of porous Vycor glass on its bulk modulus was investigated.

Measurements of adsorption expansion were made with argon and nitrogen at liquid air temperatures. The surface $^{-}$OH groups were replaced by methoxy groups. It is believed that about 70–80% of the —OH groups were replaced.

Adsorption isotherms and expansion curves showed marked differences between the methylated and unmethylated glass. The bulk moduli calculated from expansion data differed by 20–25%; the lower values being those of the methylated glass. The higher value of the bulk modulus for the unmethylated adsorbent may be explained by the fact that most of the $^{-}$OH groups present on the surface are hydrogen bonded

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Molar polarisations in the adsorbed state

D. FIAT, M. FOLMAN AND U. GARBATSKI, *Department of Chemistry, Technion — Israel Institute of Technology, Haifa*

The dielectric properties of NH_3 and CH_3OH adsorbed on porous Vycor glass were investigated using precision apparatus described previously [1].

Relying on Onsager's equation and treating the adsorbate-adsorbent system as a solution, relationships were derived which enabled us to calculate the molar integral and differential polarisations of the adsorbate.

The molar differential polarisations versus surface coverage show maxima at $\Theta = 0.15$ for NH_3 and $\Theta = 0.5$ for CH_3OH.

The substitution of methoxy groups for the hydroxy groups present on the surface causes a great change in the results obtained. It indicates that the high values of the molar differential polarisation were due to hydrogen bonding between these groups and the adsorbed molecules. The existence of such hydrogen bonding was shown elsewhere [2].

The molar differential polarisation of the adsorbates increases with increase in temperature for small surface coverages ($\Theta \approx 0.10$). For higher coverages a decrease is observed.

Comparison of the molar differential polarisations of adsorbate with the corresponding values for the gas and liquid phases shows that they depend on the strength of the hydrogen bonds formed.

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The method of "isopotential naphelometry" and its application to the study of intramolecular phase-transitions in polymethacrylate salts

I. Michaeli, *Polymer Department, The Weizmann Institute of Science, Rehovoth.*

Recently published data [1] on the critical concentrations of $Na^{\pm}$ Polymethacrylate, NaCl and $CaCl_2$ in aqueous solution at the point of precipitation suggest a hitherto unknown phenomenon of an intramolecular phase transition due to the interaction between the carboxylate and Ca^{++} ions. However a complete picture of the prevailing thermodynamic conditions cannot be obtained fron the customary presentation of the phase-separation data in terms of bulk concentrations, since in these systems the concentrations of the small ions do not represent the chemical activities even to a rough approximation.

The present investigation, therefore, deals with the phase separation behaviour in terms of chemical potentials. For this purpose, the nephelometric determination of the precipitation point is determined, using the technique of "isopotential nephelometric titration": The polymethracrylic acid, neutralized with NaOH to a given degree α, is equilibrated through a semipermeable membrane with an external "infinite" reservoir containing an aqueous solution of NaCl and $CaCl_2$ at constant temperature. The thermodynamic analysis shows that, for sufficiently high polymer concentrations in such an experimental set up, the precipitation of the polymer with a given degree of neutralization α, is a function of the concentrations of $CaCl_2$ and NaCl in the external bath only, and is independent of polymer concentration The critical conditions may thus be presented in plots of the external concentration of $CaCl_2$ at the precipitation point as a function of α, at constant concentration of external NaCl.

The experimental results thus obtained are shown to obey the suggested solubility product relation: $\mathbf{a}^{Ca^{++}} . \alpha^2$ = constant, where $\mathbf{a}$ Ca^{++}, the chemical potential of the Ca^{++} ions in the external solution, is shown to equal that of the internal solution. The above solubility constant is found to be independent of the external concentration of NaCl over a wide range of concentrations and the effect on the critical concentrations of $CaCl_2$ is accounted for by changes in activity factors.

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The study of free counter diffusion by a new light absorption method employing. photoelectric scanning

NEHEMIA SHAVIT AND RAM G. MOHAN, *Department of Polymar Research, The Weizmann Institute of Science, Rehovoth*

Diffusion experiments in certain systems containing three components are known to indicate coupling between the flows of the two solutes. It seemed to us to be of interest to extent the diffusion studies to systems in which the concentration gradients of the solutes are in opposite directions and simultaneous counter diffusion process is therefore to be expected.

For the detailed investigation of the possible interaction of such counter flows in free diffusion systems the concentration distribution of each solute has to be determined. The conventional optical methods, based on refractometry or interferometry, give only the sum of the concentrations or the concentration gradients of all solutes at any level in the cell. However, in systems where each solute has an absorption region in which no other component absorbs additional data can be obtained by light absorption measurements at suitable wave lengths.

Preliminary experiments using photographic photometry were found to be inaccurate and unreliable. A new photometric-photoelectric scanning system was developed and attached to the Tiselius-Schlieren apparatus. Difficulties due to non-uniformity in the sensitivity of the photo-cathode of the photomultiplier were overcome by an optical device. Measurements of the concentrations at any strata in the diffusion column are accurate to within 0.5%.

The system CO^- hemoglobin – bovine serum albumin — water was studied under conditions of counter flow of solutes. The concentration distribution of the CO^- Hb was measured by the new scanning system at $\lambda = 5461$ A. The concentrations of BSA were calculated by difference from the Schlieren total concentration data and the light absorption data on CO^- Hb.

The main and cross-term diffusion coefficients for this system were evaluated.

Industrial Chemistry

First Session, October 10, 1960 Chairman : H. E. HEIMANN

The analog computer in the chemical industry

A. RAVIV, *The Weizmann Institute of Science, Rehovoth*

In the field of chemical industry, the optimum process variables (concentration, temperature, pressure, etc.) are so adjusted as to lead the reaction to the desirable quality of the end-product in the least possible time and at the lowest cost. The determination of these optimal conditions of the process variable was done in the past by calculating the reaction rate — if the reaction rate constants were known — or by trial and error experiments. Both methods entailed extensive loss of time due to the complexity of some reactions and of their relevant manual computing by the classical methods (difference and differential equations of higher order).

The analog computer[1] is based on the operation of high-gain D.C. amplifiers which are capable of integration by simulation. This gives us the advantage of shortening the necessary computing time, and also the elimination of a great number of experiments of long duration in the plant, out of which we are actually interested in only one or two.

Three cases of simulation with the aid of the analog computer are reported.

1. The decay of plutonium^{242} in an atomic pile with a flux of 10^{13} n/cm^2/sec into Americium and Curium isotopes. The concentrations of the products evolving during 4 years of radiation in the pile are calculated in a matter of half a minute with the help of the analog computer.

2. A study of the kinetics of a batch reactor for the chlorination of benzene which enables us to evaluate the optimum reaction temperature and the chlorine quantity necessary to obtain a given product concentration mixture.

3. Control of a batch hydrogenation of cottonseed oil in oleo-margarine manufacture[2], with help of an analog computer. Samples of the intermediate product in the reactor are taken intermittently, fed to the computer which computes the optimal process variables (hydrogen pressure, reaction temperature, etc.) in order to shorten the reaction time and give the final product concentration desired

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Stage-by-stage calculations of multicomponent distillation columns

V. KLEIN, *Israel Atomic Energy Commission, Rehovoth and* A. RAVIV AND Z. FRAENKEL, *The Weizmann Institute of Science, Rehovoth*

Because of the large number of stages required in the separation of isotopes, stage-by-stage calculations of multicomponent mixtures cannot be made by hand or with a calculating machine, and an electronic computer has to be used.

Difference equations for the computation of concentration gradients were derived. The calculations can easily be made from the lower to the upper end (i.e. feed point) of the cascade, but iterations are needed if the computations are started from the feed point. The particular case of the separation of the isotopes of oxygen by distillation of water was investigated. Computations were done on the Weizac electronic computer.

Two problems in particular were treated in more detail.

1. Given a column with a certain number of plates, a certain flow and fixed top concentrations, what will be the bottom concentrations for a certain production.

2. Given a column with a fixed number of plates, and water of given average concentrations of O^{18} and O^{17}, what will be the final isitope concentrations at the top and the bottom of the column, and what is the maximum concentation of O^{17} if the column is operated at zero production.

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On packed distillation columns

D. MERANDA AND A. RAVIV, *Israel Atomic Energy Commission, Rehovoth and The Weizmann Institute of Science, Rehovoth*

The aim of this work was to elucidate the problems involved in the separation of isotopes [1,2] by fractional distillation in packed columns.

The research was carried out on 1″–30″ columns packed with Dixon rings of $^{1}/_{4}$″, $^{1}/_{8}$″ and $^{1}/_{16}$″ diameter. The columns were used as enrichers only.

The column hold-up, due to the vapor velocity affects the efficiency of separation and the time taken to reach equilibrium.

In all experiments conducted at varying pressures but equal percentages of flooding velocity, the hold-up per unit of volume of packing was found to be constant. This indicates that similar operation conditions exist in columns operating at various pressures but at equal percentages of flooding velocity.

According to the H_2O^{18}/H_2O^{16} and H_2O/D_2O separation results in a column with zero production, there is a constant ratio between the logarithms of the enrichments of D_2O and H_2O^{18}. From this and additional data we calculated the number of theoretical plates and found them to be equal for both separations. This fact indicates that the mechanism of separation of H_2O/D_2O and of H_2O^{18}/H_2O^{16} is identical. The number of plates is equal to the number of elementary evaporations on the packing, and therefore we can say that the separation is vertical only. In addition, from the data available in the literature[3] we found that the ratio $\frac{\alpha_o^{18}-1}{\alpha_D-1}$ (α = relative volatility) is constant at various pressures.

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Separation of minerals by heavy liquid (TBE) cyclone

A. Mitzmager and J. Mizrahi, *Israel Mining Industries Laboratories, Haifa*

The availability of cheap TBE** from the Dead Sea and its introduction in the mineral dressing field [1,2] as a heavy liquid for sink and float industrial separations required a number of chemical engineering developments in the various steps of the process. The liquid cyclone was found to be the most convenient device for the separation of fine particles.

An extensive research program was conducted in order to correlate the cyclone capacity and separation efficiency with the following variables: feed pressure, liquid sp. gr. and viscosity, cyclone geometry, particle size distribution and slurry composition. On the basis of the data collected, a method of correlation and a "standard test" were developed in order to design specific cyclones for the different applications.

A special objective was the separation of minerals very close in sp.gr. (0.01-0.05 unit differences) as, for instance, the natural constituents of pegmatite rocks (feldspars, quartz, mica, garnet, beryl etc.). Some of these minerals are valuable and their recovery attractive [3]. The separation of the various constituents of Eilat pegmatites was performed on semi-pilot-plant-scale.

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** TBE — Tetrabromoethane (*sp. gr.* 2.96).

An evaluation of polyethylene as a constructional material for use with tetrabromoethane (TBE)

E. NEVIES, D. SHERMAN AND R. BLUMBERG, *Israel Mining Industries Laboratories, Haifa*

As part of a programme of work for evaluating construction materials to be used in the manufacture of tetrabromoethane (TBE), and in its utilization as a heavy liquid in the mineral dressing industry, polyethylene was examined with a view to its use both as a liner and for the actual fabrication of units of equipment. Compatibility tests of various grades of polyethylene, including welded specimens, with media of TBE and TBE containing bromine (up to 100 g Br_2/l) yielded results which showed high chemical resistance and dimensional stability. Test periods up to 12 months involving total and partial immersion tests both at ambient temperature and at 40°C were effected, close attention being paid to textural variations and variations in mechanical strength. Similar work with media consisting of TBE in admixture with various hydrocarbons (aliphatic and aromatic) showed initial dimensional changes which soon however reached equilibrium.

Industrial Chemistry

Second Session, October 10, 1960 Chairman: Z. ZUR

Concentration of phosphate rock; a review of Israel patents with special regard to a process developed at Fertilizers and Chemicals, Haifa

A. STRAUCHEN, *Fertilizers and Chemicals, Haifa*

The native Israel phosphate ore ex-mines contains on the average 30–45% calcium carbonate. As most fertilizer manufacturing processes are based on acid treatment of rock phosphate, $CaCO_3$ is not only a balast diminishing the grade of the rock, but also consumes acid to a significant extent.

For these reasons the concentration of the raw phosphate becomes an urgent problem.

15 Israel patents cover a variety of beneficiation methods.

The raw phosphate concentration methods used currently in Israel are based on two patents, 1) mechanical differentiation and
2) flotation.

Electrostatic concentration methods seem promising, but for phosphates they are not yet finally developed.

Calcination is made use of by several patents, differing mainly by the way the CaO formed is removed. This method has been under consideration for several years.

A number of patents relate to chemical beneficiation. Briefly, these methods are based on selective leaching of $CaCO_3$ by various reagents.

A process developed by the staff of Fertilizers and Chemicals is based on treatment of the phosphate rock with hydrochloric acid. One batch of a calciferous phosphate ore is dissolved in HCl, and the $CaCO_3$ of another batch of the same rock reprecipitates the dissolved phosphate. The product obtained consists of a mixture of original apatite, tri- and/or di-calcium phosphate.

Precipitation of copper by lime as an alternative to cementation

O. Schächter, *Israel Mining Industries Laboratories, Haifa*

Copper is won at Timna by treatment of leach liquor with iron. The "cement copper" thus produced contains about 70% copper metal on dry basis, the main impurities being iron and iron oxide, alumina, silica and phosphate. Part of the copper is oxidized. At present cement copper is exported as such, but plans are being considered to melt and refine it on the spot.

In the process about 5000 m^3 effluent liquor, containing ferrous sulphate and other soluble salts, are disposed of daily. This constitutes a problem both from the point of view of pollution and water conservation.

Work has been done on an alternative approach: precipitation by lime. In this process a concentrate containing 18–20% copper is obtained (on dry basis). The filtrate can be recycled to the washing section of the plant. From the filter cake copper can be dissolved with sulphuric acid, copper sulphate can be crystallized and metallic copper won by electrolysis. The sulphuric acid obtained is recycled for solution.

The chemistry, operation and economics of the process are described and possible flow-sheets discussed, some of which are based on a different sequence of operations.

Caustification of potassium and sodium chlorides with calcium hydroxide, employing phenol for increasing the solubility

D. Araten and O. Schächter, *Israel Mining Industries Laboratories, Haifa*

The use of calcium hydroxide as a primary source of OH′-ions, both for direct caustification and using ion exchange resins, has been limited as a result of the low solubility of this material.

In a previous lecture[1] we reported the conversion of potassium chloride into potassium hydroxide with calcium hydroxide with the aid of an ion exchange resin.

In order to lower the water requirements of the process, we examined the possibility of using phenol, which increases the solubility of calcium hydroxide about sixteen times. The intermediary formed, calcium phenolate, was found to behave in aqueous solution as pure calcium hydroxide.

The conversion of potassium chloride into potassium hydroxide proceeds according to the following equations:

Loading: $R_2\text{–}Ca + 2\ KCl \longrightarrow 2\ R\text{–}K + CaCl_2$
Regeneration: $2\ R\text{–}K + Ca(OC_6H_5)_2 \longrightarrow R_2\text{–}Ca + 2\ KOC_6H_5$

(R being the resin radical)

Carbonation of the potassium phenolate solution with CO_2 decomposes it into potassium bicarbonate and phenol; the latter is virtually completely recoverable by conventional means, so that the $KHCO_3$ — solution obtained contains (at the most) 30 mg phenol/1.

Sodium chloride behaves analogously.

REFERENCE

1. Given at the 3rd convention of Scientific Societies of the Association for the Advancement of Science in Israel, held in Qiryat HaTechnion, Haifa, on the 21st of October 1959; lecture abstracted in *Bull. Res. Council Israel*, **8A.** (1959) No. 3, 27.

Preparation of potassium sulphate[1] from potassium chloride and sulphuric acid by extraction with an organic solvent[2]

J. CEITLIN AND R. BLUMBERG, *Israel Mining Industries Laboratories, Haifa*

A continuous process has been developed for the preparation of potassium sulfate from potassium chloride and sulfuric acid at room temperature.

The process depends upon the extraction of hydrochloric acid by an organic solvent from an aqueous system containing H^+, K^+, Cl^-, $SO_4^{=}$ ions. By this means the equilibrium expressed by the equation:

$$2\ KCl + H_2SO_4 \rightleftarrows K_2SO_4 + 2\ HCl$$

is disturbed and the reaction proceeds to the right.

Potassium sulphate equivalent in quantity to the HCl extracted is obtained directly as the stable solid phase. The initial composition of the mother liquor is maintained by feeding quantities of KCl and H_2SO_4 stoichiometrically equivalent to the K_2SO_4 and HCl removed.

The solvent is washed countercurrently with water to remove the hydrochloric acid, and recycled to the extraction circuit after partial dehydration.

The HCl removed from the solvent is obtained as an aqueous solution and forms the by-product of the process.

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2. Part of a doctorate thesis presented by J. Ceitlin to the Senate of the Technion under the guidance of Professor H. Heimann.

Industrial Chemisrty

Third Session, October 10, 1960 Chairman: D. Vofsi

Production of inorganic fluoride compounds

Simcha Harel, *Fertilisers and Chemicals, Haifa*

In the manufacture of superphosphate and phosphoric acid, part of the fluorine from the rock phosphate escapes as SiF_4. By absorbing this in water, fluosilicic acid which can be used for the production of various fluoride salts is obtained. The relatively insoluble sodium and potassium silicofluorides are produced by Fertilizers and Chemicals Ltd. Valuable silicofluorides of high solubility are the ammonium, magnesium and zinc salts.

By decomposing fluosilicic acid or a salt with ammonia, a suspension of amorphous silica in a fluoride solution is obtained, e.g.,

$$K_2SiF_6 + 4\ NH_4OH = 2KF + 4\ NH_4F + Si(OH)_4.$$

After filtration, the fluoride solution can be used for production of hydrofluoric acid or fluoride salts without the use of mineral acids.

By reacting fluosilicic acid or ammonium silicofluoride solution with ammonia, ammonium fluoride solution, which can be used as raw material in the production of synthetic cryolite, is obtained.

Pulp from corn stalks*

M. Lewin and A. Lengyel, *Institute for Fibre and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

An investigation on the chemical utilisation of cornstalks for the production of pulp and paper is presented.

The pulping behaviour of depithed leaf-free cornstalks, leaves and mixtures of varying composition of stalks and leaves are studied. Yields, permanganate numbers, screenings, consumptions of chemicals, freenesses, rates of beating, bulks, tear and burst factors, breaking lengths, fold numbers and porosities of the pulps obtained in the various trials were determined.

The different nature of the leaves and of the pulps obtained therefrom, as compared to the leaf-free cornstalk pulps, is pointed out and their detrimental influences on the yields and strength properties of the pulps are evaluated and discussed.

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* The study of which this paper present a brief abstract constituted a part of the work for which the authors were awarded the International Habif Prize of the University of Geneve, Switzerland, on the occasion of its 400 year Anniversary.
The authors gratefully acknowledge the grant of Mr. Joseph M. Mazer, New York, U.S.A., Dr. Astore Mayer, Milano and American Israeli Paper Mills, Hadera, Israel, which greatly aided in the carrying out of this research,

The relative merits of the sulphate (Kraft) and alkali (soda) processes with regard to the cornstalks are compared.

The influence of the varying amounts of parenchymateous non-fibrous matter of the pulps on their freenesses and other properties is determined and discussed, emphasising the importance of washing (classifying) the pulps in proper equipment.

The basic differences between cornstalks and bagasse are shown and the inadequacy of the bagasse depithing technology when applied to cornstalks is clearly proved.

It is shown that in order to obtain workable pulps from the original leaf-containing cornstalks two approaches are possible:

1. Cooking the undepithed or conventionally depithed material, followed by classifying.
2. Effective removal of the pith and parenchymateous material prior to cooking (cleaning), thus increasing yields and decreasing chemical consumption.

Two methods of cleaning are presented, one based on presteaming and refining and the other on presteaming and disintegrating. The respective merits of both methods are evaluated and compared to conventional depithing, cooking of indepithed leaf-containing and leaf-free stalks.

Cleaning of leaf-containing cornstalks by the new presteaming and refining method followed by hot alkali cooking yields 20% of pulp calculated on the weight of the original bales, and 53% of the cleaned material, with freenesses of 340–400 mls C.S.F. having at the unbeaten state tear factors of 90–100 grams, burst factors of 35–55 kgs, breaking lengths of 5000–6500 meters and M.I.T. folds of 200–700. The amount of alkali needed for producting 1 ton of pulp is 230–27 kgs, or 5% calculated on the original bales.

The presteaming cleaning methods are suggested as a suitable and industrially feasible solution of the problem of the utilisation of the cornstalks.

Bleaching of pulp from corn stalks*

M. Lewin and A. Lengyel, *Institute for Fibre and Forest Products Research, Ministry of Commerce amd Industry, Jerusalem*

Pulp was prepared from corn stalks by the alkali method, after a mechanichal separation of the fibre bundles from the pith. This pulp contained no portion of the leaves, and the separation of the pith was carried out by strong agitation of the cut stalks in water. The bleaching of this pulp by chlorine and hypochlorite in one stage and in three stages was investigated.

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The variables studied were the total amount of chlorine, its distribution between the chlorine and sodium hypochlorite stages, and the conditions of the intermediate sodium hydroxide extraction.

By a one stage bleach with 5% chlorine as hypochlorite at pH 7.8–8.0 a degree of brightness of 70% may be reached, whereas in three stages 80% brightness may be achieved.

The viscosity of the bleached pulp, was 20–30$^{\text{C.P.}}$.

The total amount of chlorine required to reach 80 % brightness in 3 stages is 5 %. Better results are obtained if the quantity of chlorine consumed is equally distributed between the chlorination and hypochlorite stages, with an intermediate sodium hydroxide extraction stage at 60°C for 1 hour.

Bleaching experiments on a larger scale, which enabled the determination of loss of strength of the pulp during the process, were also carried out.

Corn pith as a raw material for papermaking*

M. Lewin and A. Lengyel, *Institute for Fibre and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

Corn stalks contain fibre bundles which may be separated and used for making paper pulp. Apart from this the stalks contain a parenchymateous tissue comprising 23–30% of the total weight. If the pith is processed together with the fibre bundles into chemical pulp, it forms small particles with thin walls which reduce the filtrability of the pulp. For this reason it is necessary to separate mechanically the pith from the fibrous parts. The separated pith may be mechanically ground, and the fine powder obtained may be added to paper stock made from any fibrous material. The pith becomes attached to the fibres and enhances their qualities, mostly as regards opaqueness and absorption of ink.

Adding the ground pith reduces the tensile and bursting strength but increases tearing strength, stiffness and the specific volume of the paper. The dependence of these properties on the quantity of ground pith added and on the degree of grinding at equal weight percentages was investigated.

Decreasing the particle size of the pith causes a decrease in the folding endurance, in air permeability and in the specific volume and increases the retention of the tearng, bursting and tensile strengths.

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In the case of board weight sheets the specific pith contribution ratios defined as change in the ratio of the given property, when 1% of pith is added, are positive for flat crush, ring crush and tearing strength and negative for tensible and bursting strengths.

Cooking of pith at 160°C with 6% and 16% of alkali produces yields of 79% and 35% with permanganate numbers of 21.6 and 13.1 respectively.

The strength characteristics of blends of cooked pith with pulp are entirely different from those of uncooked pith: there is at all levels of cooked pith additions a positive and higher contribution of the pith to the bursting and tensile strengths and folding endurance but a lower contribution to the tear factor and specific volume than in the case of uncooked pith.

Newspring, corrugated medium, liner boards and paperboards can be advantageously produced from blends of uncooked pith with kraft or bleached sulphite pulps.

The reaction of ethylene with dilute solutions of bromine in ethylene dibromide

A. Varsanyi, L. M. Shorr, J. Segall and O. Schächter, *Israel Mining Industries, Haifa*

The I.M.I. process for the production of ethylene dibromide (E.D.B.) is based upon the extraction of bromine from brines with E.D.B. and subsequent reaction of this relatively dilute solution with ethylene. The factors which influence this reaction, viz.: light, temperature, air and humidity, are discussed and the bench scale continuous reactor in which this study was performed is described.

Ethylene dibromide production via solvent extraction[1] — factors which influence yield and purity of product

S. Lavie and O. Schächter, *Israel Mining Industries Laboratories, Haifa*

In the extraction of bromine from Dead Sea end brine by ethylene dibromide (EDB) losses are liable to result through dissolution, emulsification and entrainment. Factors responsible for the formation of emulsions have been studied.

It was anticipated that the purity of the product under the conditions of this process would depend on the chlorine content of the bromine extracted, and on hydrolysis and reaction with chloride ions contained in the brine. It was shown that virtually no chlorine is contained in the extract. Experiments in which bromine was reacted directly with ethylene in the brine are described. The reaction between ethylene and bromine solutions in EDB forms the subject of a special lecture.

REFERENCE

1. Cf. communication to the 22nd Convention of the Israel Chemical Association, 14—15 October 1957.

Electrochemical dimerization of acrylonitrile to adiponitrile

J. Padova and D. Vofsi. *Polymer Department, The Weizmann Institute of Science, Rehovoth*

The electrochemical reduction dimerization of acrylonitrile (AN) to adiponitrile (ADN) in acid solution by means of a continuously reformed potassium amalgam has been described by Knunyants [1,2].

According to this author, the process could be represented as follows:

$$CH_2 = CHCN + \varepsilon^- + H^+ \longrightarrow CH_2 - CH_2CN$$

$$2.\ CH_2 - CH_2CN \longrightarrow NC\text{-}(CH_2)_4CN$$

Yields of adiponitrile of about 60 % in a batch operation were claimed, but influence of the various reaction parameters on the process was not reported.

When repeating Knunyant's experiments under identical experimental conditions yields of only 7–20 % of adiponitrile were received, the remainder of the acrylonitrile being converted to polyacrylonitrile. However, on addition of catalytic quantities of quinones, hydroquinones, aminoquinones, etc. yields of ADN were substantially improved. By using salts of the transition metals in combination with a quinonoid compound — in catalytic quantities — yields of up to 80 % of ADN were achieved in a batch operation, while polymer formation was completely eliminated.

A detailed parametric study of the reaction was carried out under batch and continuous flow conditions.

Reaction variables were:

Potassium concentration in amalgam
Concentration of AN
Concentration of HCl
Molar ratio AN/HCl
Catalyst concentration
Rate of flow of reactants over amalgam surface

Yields and energy efficiencies are given in terms of the above variables, and optimal conditions for the process are evaluated.

The mechanism put forward by Knunyants is criticized, and an alternative mechanism is discussed.

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Inorganic Chemistry

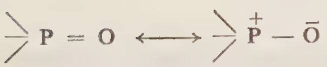
First Session, October, 1960 Chairman. K. S. Spiegler

Organic N-oxides as complexants

A. Heller, *Israel Atomic Energy Commission Laboratories, Rehovoth*

Tributyl phosphate and other esters of phosphoric acid yield complexes with uranium and plutonium which are soluble in organic solvents. In these compounds the oxygen atoms "double bonded" to the phosphorus serve as donors (I). In the analogous nitrogen compounds (II), it should be expected that because of the increased negative charge on the oxygen the donor properties would be enhanced, and that these compounds should act as complexants similar to the organo-phosphorus compounds, with still higher affinity for the uranium and plutonium cations.

Whereas compounds like (III), where R is an aliphatic group, are not stable in the presence of various cations, which precludes their use, compounds where the nitrogen is part of an aromatic system (like the pyridine-N-oxide (IV) and the quinoline-N-oxide (V)) are stable. (IV) gives a complex with the uranyl cation, as expected, which may be isolated. Since both the complexant and the complex are highly polar, they are not extracted by organic solvents. A polymer of vinyl pyridine-N-oxide (VI) was prepared, which binds the uranyl ion selectively, and permits its removal from solutions.



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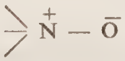

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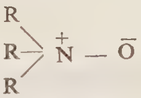
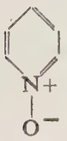


III



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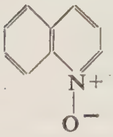
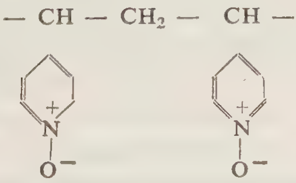


V



VI

The distribution of zinc chloride between anion exchangers of different crosslinking and electrolyte solutions

DALIA MAYDAN, *Israel Atomic Energy Commission Laboratories, Rehovoth*

The high selectivity which anion exchangers show towards many metal complexes has not yet found a complete explanation. An attempt is made towards understanding this phenomenon by studying the effects of changing the crosslinking and capacity of the resin, and the bulk electrolyte cation, on the distribution of a metal complex. The system investigated comprised zinc chloride tracer, M^+Cl^- solutions ($M^+ = Li^+$, Na^+, K^+ and NH_4^+) and exchangers of the trimethyl benzyl ammonium type, crosslinked with divinyl benzene.

The distribution coefficient D (concentration per gram resin/concentration per gram water) was measured as a function of salt molality, by adding weighed amounts of salt to a solution containing zinc, added as $Zn^{65}Cl_2$ tracer, and the resin. The solution was continuously circulated through a gamma scintillation counter, and its activity was recorded. The resin was prevented from accompanying the solution by a sintered glass filter.

For a given resin and molality, D was found to decrease in the order Li, Na, NH_4 and K. For a given solution D was found to increase with the crosslinking of the resin, but the rate of attainment of equilibrium decreased. These results, and similar published data [1, 2], are interpreted in terms of the charge density distribution in the resin. Together with previously reported results on the activities of the bulk electrolytes in these systems[3], it should be possible to obtain a complete picture of the mechanism of the reaction and the species involved.

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Difference of "invasion" of an ion-exchange membrane by monovalent and polyvolant ions in connection with the sign reversal and "poisoning" of such membranes

F. KÖRÖSY, *The Negev Institute for Arid Zone Research, Beer Sheva*

It has been shown[1,2] that ion exchange membranes may be "poisoned" by some trivalent or more highly charged ions to such an extent that their charge, i.e. the sign of their permselectivity, is reversed. This was explained by the assumption that the highly charged ions are held so strongly by electrostatic forces on the fixed ions of the resin that they effectively change the sign of its charge and the original co-ions begin to act as secondary counter-ions.

The enhanced invasion of the resin by the highly charged ions must however be proved by analytical methods. To this end pieces of anionselective membranes (parchment impregnated with formaldehyde-pyridiniu mresin) were equilibrated with a series of KCl and $K_3Fe(CN)_6$ solutions respectively, of varied concentration. After equilibrium had been attained the pieces were blotted quickly between filter paper and weighed to determine the volume of solution which remained in the membrane. In this respect it is much easier to work with membranes than with granular resins because reproducible blotting offers a great advantage. The Cl^{-1} and the $Fe(CN)_6^{-3}$ ions respectively were then quantitatively extracted with n/1 KNO_3 solution and titrated.

The concentration of $K_3Fe(CN)_6$ which was present in the membrane in excess of the resin capacity was higher than the concentration of KCl present in it in equilibrium with KCl solutions of the same normality.

When a resin with fixed monovalent positive ions is just saturated with trivalent negative $Fe(CN)_6^{-3}$ ions and is in equilibrium with pure water, then every third resin ion has found a partner. This partner may be bound to one resin ion, changing it into a divalent negative site. Electrostatic compensation comes from two adjacent empty positive sites. However the empty sites tend to bind further ferricyanide ions if such are available in the solution. Electrostatic compensation now comes from K^+ ions also which are drawn into the resin. This is the excess of $Fe(CN)_6^{-3}$ we have found in our titrations and which has also been the cause of the charge reversal of the membrane because more than one third of the monovalent sites have been occupied by trivalent counter-ions.

The question is also discussed from the point of view of the Donnan equilibrium

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An ion-exchange study of pyrophosphate and copper-pyrophosphate solutions

C. HEITNER-WIRGUIN AND J. KENDI, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

Equilibrium studies were made of some pyrophosphate solutions on anion exchangers of different water-regain. The mean charge of the pyrophosphate ion sorbed is about 4, and the relative amounts sorbed do not depend on the water-regain of the resin.

The complexes existing between copper and pyrophosphate in solutions were studied on cation and anion exchangers and their formula and charge evaluated. The eventual participation in the complex formation of a second anion is discussed.

Inorganic Chemistry
Second Session, October 11, 1960 Chairman: Y. Marcus

The relationship between water content and water partial vapour pressures in solute–water–organic solvent systems.–A new method of determining vapour pressures

A. Baniel, R. Blumberg and L. Gonen, *Israel Mining Industries Laboratories, Haifa*

In systems of solute-water -organic solvent, the relationship between water content and water partial vapour pressure (w.p.v.p) for any given solvent can be represented by a series of isotherms. At a given temperature the w.p.v.p. is uniquely determined by the water content. If a system is selected in which the organic phase contains only negligible amounts of solute and the aqueous phase only negligible amounts of organic solvent, the water content of the solvent phase is a measure of the w.p.v.p. of the aqueous solution in equilibrium with it. This relationship permits the immediate deduction of the w.p.v.p. of an aqueous solution from the knowledge of water content in the organic solvent, which is simple to determine.

The system *n*-hexanol-electrolyte-water, and octane-2-ol-electrolyte-water, were selected as reference systems, and the water content of the solvent phase accurately determined at 20°C and 40°C for a series of aqueous solutions of known w.p.v.p. At each temperature there is a straight-line correlation between w.p.v.p. and water content of solvent for a definite range of vapour pressures. These correlations can serve as a simple method for determining w.p.v.p. of aqueous solutions, particularly in the neighbourhood of ambient temperatures.

Saturation effect in the system aqueous hydrochloric acid-uranyl chloride-tri n-butyl phosphate

A. S. Kertes and M. Halpern, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

The distribution of macro-amounts of uranyl chloride between hydrochloric acid and undiluted tributyl phosphate has been examined as a function of uranyl chloride concentration in the initial aqueous solution. The pregnant organic layers involved have been investigated by means of volume-swelling determinations and viscosity, density and spectrophotometric measurements. The water content of the tributyl phosphate phases has also been determined.

It was found that it is neither the saturation effect nor the higher polymerization of uranium in the aqueous phase which operates against the salting-out effect, but rather that it is the competition between two solvates, namely the hydrochloric acid-monosolvate-trihydrate and the uranyl chloride-disolvate, which governs the extraction of uranyl chloride from aqueous solutions. Accordingly, the extraction mechanism involved is suggested.

Heterogeneous equilibria in the system aqueous nitric acid — potassium perrhenate — tri n-butyl phosphate

A. Beck and A. S. Kertes, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

The extraction of heptavalent rhenium into tributyl phosphate solutions from aqueous nitric acid solutions has been investigated as a function of solvent concentration in the organic phase and nitric acid concentration in the aqueous phase, the rhenium concentration being kept constant. The method of continuous variations has been applied to follow the formation of the extractable rhenium compound. The results revealed that perrhenic acid was the only extractable species. The solvent dependencies have been found to be direct fourth-power. The mass action effect and the anti-synergetic interaction between nitric and perrhenic acid have been used to interpret the extraction mechanism involved. An attempt has been made to calculate the formation constant of perrhenic acid-tetrasolvate.

The extraction of HCl with TBP and third phase formation

N. Rosintal and E. Foa, *Israel Atomic Energy Commission Laboratories, Rehovoth*

As part of a program of studying solvent extraction, we investigated the third phase resulting from the treatment of HCl solution with tri-n-butyl phosphate (TBP) in inert diluents. This third phase is the heaviest of the two organic layers present and is also the richest in TBP and HCl.

The third phase is formed only under certain conditions: a minimal initial HCl concentration (7M at 35°C) and a maximal temperature characteristic of each diluent. Furthermore, the use of aliphatic diluents is essential. The presence of LiCl decreases the amount of HCl required.

As long as third phase is formed, the HCl concentration in the organic phase rises steeply with the aqueous HCl concentration. With its formation, the distribution coefficient of the HCl is highest for the third phase. This distribution coefficient is not influenced by equilibrium aqueous HCl concentrations above 8.8M nor by the initial TBP concentration in the range 5–40%.

The concentration of TBP in the third phase is not affected by increasing equilibrium aqueous HCl concentration above 8.8 M.

Two liquid organic layers are produced also under anhydrous conditions, as is shown by bubbling HCl gas into dry TBP — diluent solutions at 10°C.

The composition of the third phase has been found to vary the aqueous HCl equilibrium concentration. At low HCl concentrations the ratio TBP to HCl is 5:3, while at high concentrations it is 2:3. The 1:1 adduct which is formed probably acts as a solvent for the excess TBP or HCl as the case may be.

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Ruthenium tetroxide in nitric acid solutions

Shiloh M., *Israel Atomic Energy Commission Laboratories, Rehovoth*

A. The oxidation of ruthenium to tetroxide, and its extraction with kerosene.

It is possible to separate ruthenium in its octavalent form, the tetroxide. This compound is volatile and soluble in organic solvents, but is very susceptible to reduction. In this work a way was found for the separation of the tetroxide by addition of sodium hypochlorite to its solution in nitric acid thereby preventing its immediate reduction on contact with the organic solvent.

The factors affecting the distribution coefficients for ruthenium tetroxide between nitric acid and kerosene were studied. The cofficient shows a maximum at $p\text{H}=7$, and decreases both at higher pH, because of reduction, and at lower pH, and continues to diminish with increasing nitric acid concentration (see below). Contrary to expectations, there is an effect of the phase volume ratio, in particular at low nitric acid concentrations probably because of reduction which is greater the higher the amount of organic material present. It is possible to prevent the reduction by making the solutions at least 0.1 N with respect to sodium hypochlorite.

B. The behaviour of ruthenium tetroxide in nitric acid.

Experiments were carried out to test the hypothesis that ruthenium tetroxide in nitric acid attains the equilibrium:

$$\text{RuO}_4 + \text{H}^+ \leftrightharpoons \text{HRuO}_4^+$$

as proposed by Martin [1], to explain the decrease of the distribution coefficient between nitric acid and carbon tetracholride with increasing nitric acid concentrations.

1) A spectrophotometric examination of ruthenium tetroxide solutions in nitric acid of various concentrations did not show differences in light absorption that could indicate this euilibrium.

2) Electromigration experiments did not show migration of ruthenium tetroxide in nitric acid solutions under the influence of the electric field.

Since the interaction proposed by Martin could not be proved, a different explanation for the decrease in the distribution coefficient should be found. A possible cause may be the decrease in the dielectric constant of the aqueous solution with increasing nitric acid concentrations, as found for various electrolytes [2], i,e, salting in.

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Inorganic Chemistry

Third Session, October 11, 1960 Chairman: A. GLASNER

New garnet-type ferrites containing praesodymium or lanthanium*

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The rare earth ferrites with a garnet structure have a chemical formula of R_3^{+3} Fe_5^{+3} 0_{12}, where R^{3+} is a trivalent ion of the rare earth elements series from Sm^{3+} to Lu^{3+} or Y^{3+}. The lighter rare earth ions such as Nd^{3+}, $Pr^{3+}Ce^{3+}$ cannot enter this structure, having too great an ionic size[1]. However, by adding Y^{3+} to the chemical composition of the garnet Nd^{3+} could be introduced into the garnet structure up to 2/3 of the rare earth ions per unit cell[2], i.e., to a formula $YNd_2Fe_5O_{12}$.

A similar research was undertaken to establish the maximum amount of praesodimium, cerium or lanthanium which can be substituted for Nd in the yttrium-iron-garnet.

This and the sintering conditions of these garnets were investigated. The maximum value of saturation magnetization at room temperature and X-ray powder diffractions patterns were measured to determine both the maximum amount of the larger rare earth ions which can enter the garnet structure and the optimum firing temperature.

The samples were prepared according to a formula $R^{3+}_{3x}\ Y^{3+}_{3(1-x)}\ Fe^{3+}_5\ O_{12}$ where R^{3+} is Pr^{3+} Ce^{3+} or La^{3+} and x ranges from 0 to $^2/_3$.

Pure garnet phases were obtained for the following samples: the praesodimium containing samples for $x = 1/6$ and $x = 1/3$ and for the lanthanium containing samples with $x = 1/6$. The samples containing praesodimium with $x = 1/2$ and lanthanium with $x = 1/3$ and $x = 1/2$ were nearly pure phases of garnets. Only two weak X-ray lines could be indexed there as belonging to a perovskite phase with a formula of $R^{3+}Fe^{3+}O_3$ (where $R^{3+} = Pr^{3+}$ and La^{3+}). Most of the samples with $x = 2/3$ have a large amount of perovskite. The ions of cerium did not enter the garnet phase at all.

The saturation magnetization at room temperature of the pure garnet phase structure is of the same magnitude as yttrium-iron-garnet, i.e., 27± 1 cgs/gr. The samples with $x = {}^2/_3$ have much lower magnetic moments. These results were obtained for the best synthesis conditions, i.e., firing temperatures of about 1350°C for a period of about 8 hours.

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On the solubility of mixed crystals of alkaline earth nitrates in nitric acid solutions

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Some of the alkaline earth and similar nitrates are sparingly soluble in concentrated nitric acid solutions. They are deposited from such solutions in the unhydrated form. The nitrates of barium, strontium, calcium and lead are known to be isomorphous[1] and to form mixed crystals [2].

The concentration limits for mixed crystal formation of pairs of these nitrates as well as the thermodynamic activities of their components were determined by solubility measurements using radioactive tracers.

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Tracer experiments on the pyrolytic decomposition of $KClO_4$, $KClO_3$ and $KBrO_3$

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$KClO_4$, $KClO_3$ and $KBrO_3$ wre crystallised from solutions containing ions highly enriched in O^{18} (92% O^{18} and ions of normal isotopic compisition. The mixed crystals were decomposed in sealed ampoules and the isotopic composition of the evolved oxygen was determined. If the decomposition would yield molecular oxygen from a single KXO_n molecule, a mixture of $O_2^{16,16}$ and $O_2\ ^{18,18}$ would result. It was found that in the pyrolytic decomposition of all three salts ($KClO_4$ at 500°C, $KClO_3$ and $KBrO_3$ at 395°C) totally scrambled oxygen if formed. When these salts were catalytically decomposed with MnO_2 at lower temperatures ($KClO_4^{18}$ at 390°C; $KClO_4^{18}$ and $KBrO_3^{18}$ at 290°C) no oxygen from the MnO_2 was found in the evolved gas which was scrambled again. Studying the exchange between molecular oxygen and the pyrolised salts at decomposition temperatures, no such exchange was observed for $KClO_4$ and $KBrO_3$ at 500 and 390°C respectively. $KClO_3$ on the other hand showed appreciable exchange at 390°C. $KClO_4$ exchanges slowly with O_2 at 390°C and $KBrO_3$ showed slow exchange with O_2 at 290°C; in all these cases the exchange with O_2 involved scrambling, namely breaking of the O-O bond. These results imply a similar mechanism of the decomposition of all three salts in which the X-O bonds are ruptured one at a time. The compound of lower oxidation state formed may be oxidized by molecular oxygen. MnO_2 catalyses the decomposition without forming a higher oxide in which all oxygen atoms are equivalent, but probably acts as an adsorbent for the oxygen evolved and hinders the reverse reaction.

Analytical Chemistry

October 10, 1960 Chairman: BAREL

The use of radioisotopes in the titration of halogens at low concentrations

J. YOFE, Y. WELWERT AND W. TULER, *Israel Atomic Energy Commission, Rehovoth*

This work consists of an attempt to determine quantities of chlorine, bromine and iodine at concentrations of 0.001M separately and in the presence of each other.

The chlorine and the iodine were tagged with Cl^{36} and I^{131}. The bromine was not tagged.

Increasing amounts of 0.001 M $AgNO_3$ solution were added to test tubes containing the same quantities of halogen or mixture of halogens. After some time the precipitate was filtered off and the filtrate and precipitate tested by β,or when appropriate (iodine present), by γ counting.

The volume of silver nitrate was plotted against activity of filtrate or precipitate. Using the method of leasts squares, curves consisting of straight lines were drawn. Intersection points of these lines give the quantities of halogens.

In the case of the filtrate from two active halogens, Cl^* and I^*, two downward sloping straight lines are obtained, the slopes depending on the equivalent activities. When the curves have nearly the same slope, the intersection point is difficult to find and it is then possible either to use untagged iodine which will give a line parallel to the X-axis or to add untagged bromine which will separate the two lines given by the icdine and chlorine.

The quantities of I^* and Cl^* can also be determined by β- and γ- counting, the results being obtained by difference.

Cl, Br, and I can, in this way be determined in the presence of each other be several methods.

Ethanol was added to reduce the solubility of the silver halides.

If one halogen is much more concentrated than the other (for example a small amount of iodine in the presence of much bromine) the possibility of co-precipitation is much greater. This will be investigated.

By the method described it is possible to determine quantities of half a microequivalent of each halogen.

Separation of metals as chloride complexes by anion exchange

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The selective adsorption of the chloride and fluoride complexes of tin, antimony, lead and copper on anion exchangers was exploited for their quantitative separation.

The adsorption of the complexes is a function of the concentration of the complex forming ligand, the ionic strength of the medium, and its acidity.

Conditions for separation on Amberlite - IRA-400 were chosen by reference to adsorption date for these elements available for Dowex-1. It was found that the behaviour of the four elements in the column when they were present simultaneously differed considerably from that observed when they were determined singly; the elution curves of copper, lead and antimony are shifted towards higher elution volumes.

Efficient separation could be obtained by limiting the amount of tin present and employing hydrofluoric acid to elute antimony.

The separation may be outlined as follows:

1) Adsorption of the metal chloride complexes on the anion exchanger from 7N hydrochloric acid.
2) Elution of lead with 7N hydrochloric acid.
3) Elution of copper with 1·56N hydrochloric acid
4) Elution of antimony with a mixture 1N in HF and 0·3N in HCl.
5) Elution of tin with 6N NaOH.

The maximum relative error in determination of the concentration of each element was 2% and the time consumed by the analysis was one hour and a half.

The reaction of phosphorus pentoxide with alcohols

M. Zangen, *Israel Atomic Energy Commission Laboratories, Rehovoth*

The product of the reaction $P_2O_5 + 2\ ROH$, previously assumed to be the dialkyl pyrophosphoric ester $R_2H_2P_2O_7$, was found to be a mixture of several phosphoric, and meta-phosphoric esters, the number of which depends on the structure of R.

Separation of these esters was effected by a paper chromatographic method specially adapted to this case. Complete description of this method (solvent, time, temperature, magnitude of sample etc). is given. Results obtained on mixtures of esters from various alcohols are discussed.

The heteropoly blue method for silica determination — an improvement in accuracy

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The sensitive heteropoly blue reaction was developed into a versatile and precise method for the determination of silica in various materials. Conflicting statements as to concentration ranges and accuracy are found in the literature [1,3]. Precision and accuracy are stated to be poor especially for the higher concentration ranges [2].

Good reproducibility but erratic accuracy was obtained by using a calibration curve even at the most favorable concentration range of SiO_2 (50-70% transmittance). The only way to obtain consistent accuracy was by adjusting SiO_2 solution having 62% transmittance against a blank to read 100% transmittance. All unknown samples were determined against that standard. The optimum concentration range at which the highest reproducibility and accuracy are obtained was found to be approximately 30 γ SiO_2 per 50 ml.

A Zeiss spectrophotometer PMQ II (with prismatic monochromator) was used, the transmittance being measured at 812 mμ

Soda feldspar, iron ore, lime stone, burnt refractory, boro-silica glass, metallurgical slags and cement copper were analysed for silica content by this method. Results are presented showing that precision and accurace equals those obtained by gravimetric methods, using certified samples of the N.B.S. wherever possible.

The method is being applied also for rapid visual determinations of SiO_2 in cement copper. The concentration range between 10 and 50γ of SiO_2 in 50 ml is suitable for visual determination with satisfactory accuracy.

In weakly acid solutions containing high concentrations of coloured ions (leach liquors) SiO_2 is determined after applying dialysis using a cellophane membrane.

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Influence of chloride ions on the nitrate determination by Leithe's method

C. Heitner-Wirguin and D. Friedman, *Department of Inorganic aud Analytical Chemistry, The Hebrew University of Jerusalem*

Using the method described by Leithe, it appeared that if the ferrous solution was boiled with different amounts of chloride ions (up to a certain concentration) different amounts of dichromate had to be used for the titration. This influence was studied from the analytical as well as from the general chemical point of view.

2,2′-Dithio-diethyl svlphide as an analytical reagent for nickel

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2,2′-Dithio diethyl sulphide (D.D.S.) was found to be a valuable quantitative reagent for the analysis of Ni^{**} in the presence of many of the common ions. Nickel in aqueous solution in the presence of ammonia is treated with D.D.S. dissolved in an organic solvent and extracted into the solvent phase. The red color obtained is measured spectrophotometrically at 520 mμ. An accuracy of 2–3% relative was obtained on standard steels.

The characteristics of the reagent and the analytical method will be described.

Titration of carbonate — bicarbonate buffer solutions

M. Zangen, *Israel Atomic Energy Commission Laboratories, Rehovoth*

The acidimetric titration as generally used in analysis of carbonate/bicarbonate was found inaccurate whenever the concentration ratio carbonate/bicarbonate was very different from unity.

The pH at the equivalent point for the carbonate varied over the range 7.9 – 9.1 as a function of the initial concentrations.

These facts limit the usefulness of the acidimetric titration in this case to the determination of total alkalinity. For determination of carbonate and bicarbonate use can be made of a graph giving iso-*p*H curves as a function of carbonate bicarbonate concentrations.

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Section A

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INDEX

TO

VOLUME 9A

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INDEX
TO
VOLUME
9A

CONTENTS

Numbers 1—2, April 1960

Hydrolytic activity of chlolinesterases at low substrate concentrations, correlated with the biological effectiveness of choline esters .. ..*M. Wurzel* 5

Enzyme systems in adipose tissue participating in fatty acid esterification .. .. *G. Rose and B. Shapiro* 15

Proteolytic activity of chicks' intestines .. ..*Z. Nitsan and E. Alumot* 23

Cellbound penicillinase and exopenicillinase in the γ-state .. .. *N. Citri* 28

2-Guanidoethyl thiosulphuric acid .. .. *A. Kaluszyner* 35

A comparative study of ion-exchange equilibria in triphosphate and copper triphosphate solutions .. .. *C. Heitner-Wirguin* 37

Paper chromotography of 2,4-dinitrophenyl hydrazones of aromatic ketones .. .. *E. Breuer, H. Leader and S. Sarel* 43

Antimetabolic activity of amino alkyl sulphonic acids and their derivatives .. .. *P. Moses, J. Mager and M. Frankel* 46

Resolution of N-benzyl-DL-aspartic acid .. *Y. Liwschitz, A. I. Vincze and E. Nemes* 49

Proceedings of the XXVIth scientific meeting of the Israel Chemical Society 55

Glutamine synthetase and glutamotransferase in sheep liver enzyme preparations .. .. *J. Greenberg and N. Lichtenstein* 125

Optical rotatory dispersion and viscosity changes accompanying the forward and reverse mutarotation of poly-L-proline in solution .. .. *I. Z. Steinberg, M. Sela, W.F. Harrington, A. Berger, E. Katchalski* 130

Helix-coil transition of poly-L-glutamic acid in a chloroethanol-water mixture .. .. *L. Goldstein and E. Katchalski* 138

Water soluble forage constituents and their influence on the metabolic activity of the rumen .. .. *A. Bondi and H. Tagari* 143

A *p*H-static method for the assay of arginase .. .. *M. Rigbi* 149

LETTER TO THE EDITOR

Studies on the chemical composition of pollen from *Pinus canariensis* .. .. *E. Havivi and J. Leibowitz* 157

Numbers 3—4, November 1960

The thermal hydrolysis of metal chlorides, II. Cobaltous chloride and manganous chloride .. ..*A. Glasner and I. Mayer* 161

The influence of some volatile elements on the intensities of spectral lines of Sm. Eu. Gd and Dy in the DC arc .. .. *Sima Held* 173
Equilibrium studies in the system KCL-HCL-nBuOH-H_2O .. .. *R. Blumberg, P. Lewi and P. Melzer* 177
Metal ketyls as initiators of polymerization of vinyl monomers. Polymerization of acrylonitrile, styrene and methyl methacrylate by disodium benzophenone .. .. *A Zilkha, P. Neta and M. Frankel* 185
Organic fluorine compounds, Part XVIII. The reaction of diethyl oxalofluoroacetate with aromatic hydrocarbons .. .. *I. Shahak and E.D. Bergmann* 193
Specific ionic effects on reaction rates: the reaction between bromoacetate and hydroxyl ions .. .. *Miryam Bobtelsky, B. Perlmutter-Hayman and G. Stein* 195
An approximate treatment of the kinetics of reversible parallel reactions .. .. *Assa Lifshitz and B. Perlmutter-Hayman* 200
The synthesis of dl- and d-podocarpan-6-one, potential intermediates for the synthesis of diterpenes .. .. *F. Sondheimer and M. Gibson* 204

LETTERS TO THE EDITOR

The thermal decomposition of ammonium perchlorate in the presence of magnesium oxide .. .. *A. Hermoni (Makovky) and A. Salmon* 206
The pulse technique in the isotope separation by electromigration .. *Michael M. Benarie* 207

BOOK REVIEWS

Heterocyclic Chemistry, An Introduction .. .. *M. Frankel* 209
Chromatographic Reviews, Progress in Chromatography Electrophoresis and Related Methods .. .. *M. Frankel* 209
The Enzymes .. .. *E. Ellenbogen* 210
Proceedings of the XXVIIth meeting of the Israel Chemical Society 215

AUTHOR INDEX

A
Alumot. E., 23
Anbar, M., 69 221, 223, 224, 252
Araten, D., 238
Ariel, N., 254
Arnon, R., 111, 112
Ascarelli, I., 110
Ashkenazy, I., 115
Avi-Dor, Y., 99, 105
Avron, M., 99

B
Baniel, A., 68, 248
Bar-Eli, A., 101
Bar Eli, K., 220
Beck, A., 249
Benarie, M. M., 207
Ben-Efraim, S., 113
Ben-Ishai, D., 55
Bentov, M., 87
Ben-Zvi, R. 93
Berger, A, 130
Bergmann, E.D., 71, 76, 78, 79, 81, 85, 107, 193
Bergmann, F., 73, 74, 94, 96, 97, 106
Bernas, B., 254
Bichowsky-Slomnicki, L., 109, 113
Bien, S., 82
Blauer, G., 215
Blum, J., 85
Blumberg, R., 237, 239, 248
Bobtelski, M., 195
Bohak, Z., 119
Bondi, A., 110, 143
Bracha, P., 79
Breuer, E., 43, 77
Brockson-Fuchs S., 83
Budowski, P., 110

C
Cais, M., 80
Ceitlin, J., 239
Chari-Bitron, A., 109
Citri, N., 28, 104
Cohen, S., 71
Cohn, H., 70

D
Daniel, E., 116
Daniel, V., 122
Danon, S., 116
Dikstein, S., 95

E
Eden, C., 229
Ellenbogen, E., 119
Elson, D., 123
Epstein, J. A., 226

F
Feilchenfeld, H., 229
Felkman, M., 123
Fiat, D., 231
Foa, E., 249
Folman, M., 217, 231
Fraenkel, Z. 235
Frankel, M., 46, 56, 59, 65, 185, 209, 210
Friedlender, A., 68
Friedmann, N., 111

G
Galun, A., 80
Garber, N., 104
Garbatski, U., 231
Gat, J.R., 252
Gatt, S., 87
Gertner, D., 65, 66
Gibson, M., 204
Glasner, A., 161
Globerson, A., 123
Goldfarb, A.R., 121
Gonen, L., 248
Greenberg, J., 125
Grodzinski, J., 228
Gromet-Elhanan, Z., 94
Guggenheim, K., 111
Guttman, S., 220, 223, 224

H
Halevy, S., 111
Hestrin, S., 91
Hoffmann, E., 121

J
Jawetz, P., 229
Jeselson, M., 230
Jortner, J., 216

K
Kalmus, A., 73, 74
Kaluszyner, A., 35, 107
Katchalski, E., 35, 63, 65, 66, 101, 116
Katchalsky, A., 228
Katzir, A., 230
Kaufmann, E., 95
Kaye, A.M., 121
Kendi, J., 247
Kerpel, S., 90
Kertes, A.S., 223, 248, 249
Kindler, S.H., 99
Kirowa, E., 254
Klein, F.S., 220
Klein, J., 62, 78
Klein, V., 235
Knobler Y., 56, 59
Korösy, F., 114, 246
Koshland, Jr., D.E., 100
Kowarsky, H., 72
Kozirovski, V., 231
Kwietny, H., 74, 94, 97

L
Lapidot, A., 225, 226
Lapidot, Y., 63
Lavie, D., 72
Lavie S., 243
Lawson, W.B., 61
Leader, H., 43
Leibowitz, J., 92, 157
Lengyel, A., 240, 241, 242
Levin G., 73, 74
Levy, H.M., 100
Levy, M., 215
Lewin, M., 226, 227, 240, 241, 242
Lewi, P., 177
Lichtenstein, N., 125
Lifschitz, A., 200, 217, 222
Lifschitz, C., 218, 219
Linschitz, H., 215
Littauer, U.Z., 122
Liwschitz, Y., 49, 55

M
Mager, J., 46, 98
Marcus, D., 69
Maydan, D., 246
Mayer, P., 177
Meir, A., 62
Meitzler, D., 227
Melzer, P., 177
Meranda, D., 235
Michaeli, I., 230, 232
Mitzmager, A., 236
Mitzrahi, J., 236
Modiano, A., 80
Mohan, R.G., 233
Moses, P., 46

N
Nemes, E., 49
Neta, P., 185
Neumann, H., 102, 103
Nevies, E., 237
Nitsan, Z., 23

O
Ohad, I., 91, 116

P
Padover, J., 244
Patchornik, A., 61
Pelchowicz, Z., 82, 83, 84
Perlmutter-Haymann, B., 195, 200, 217, 222
Pinchas, S., 216
Pohoryles, L.A., 69. 86, 108

R
Rabani, J., 219
Rabinowitz, M., 78
Rabinsohn, Y., 55
Ramot, B., 115
Raviv, A., 234, 235
Rein, R., 69
Rigbi M., 105, 149
Rimon, A., 115
Rimon, S., 106
Rogozinski, M., 68
Ron, A., 217
Rose, G., 15, 89
Rosintal, N., 249

S
Sadeh, T., 64, 65
Salmon, A., 206
Samuel, D., 225, 226, 228
Sarel, S., 43, 68, 69, 72, 77, 86, 108
Schächter, O., 238, 243
Scheiber, M., 251
Schmorak, J., 227
Schnepp, O., 215, 217
Schramm, M., 92, 93
Segall, J., 243, 255
Sela, M., 103, 104, 111, 112, 130
Selinger, Z. 92
Shafrir, E., 90
Shahak, I., 85, 193
Shalitin, Y., 101
Shapiro, B., 15, 90, 91
Shasha, B., 92
Shavit, N., 230, 233
Sherman, D., 237
Sheradsky, T., 56, 59
Shiloh, M., 250
Shorr, L.M., 68, 70, 243, 255
Shvo, Y., 72
Silberman, Z., 215
Silver, B., 227
Sondheimer, F., 204
Steinberg, I.Z., 118, 130
Strauchen, A., 237

T

Tagari, H., 143
Tal, M., 123
Tietz-Devir, A., 88
Treinin, A., 216
Tuler, W., 253
Tzur, R., 91

U

Ungar, H., 94, 96, 97

V

Varsanyi, A., 68, 70, 243, 255
Vincze, A. I., 49
Volfsi, D., 228, 244
Vromen, A., 254

W

Weiss-Broday, M., 226
Weiss-Zehavi, M., 98
Welwert, Y., 253
Witkop, B., 61
Wolman, Y., 101
Wurzel, M., 5

Y

Yagil, C., 220
Yaron, A., 117
Yaroslavsky, S., 76, 81
Yofe, J., 254

Z

Zangen, M., 254, 256
Zehavi, U., 55
Zilka, M., 185

SUBJECT INDEX

A

Absorption intensity of $X=0^{18}$ groups stretching bands, 216
Acetobacter xylinum, washed cells of, 116
Acetylene, the reaction of, with solutions of bromine tetrabromoethane (TBE), 70
Acridine orange
  influence of polyelectrolytes on absorption spectra of, 215
  in solution, flash-excitation of, 215
Acrylonitrile to adiponitrile, 244
Action of X-rays on aqueous solutions of ferro-ferricyanide, 219
Acyloin rearrangement, on the Oumnova, 68
Adipose tissue
  enzyme systems in, 15
  fatty acid esterification in, 89
  in relation to fat mobilization, 90
Aerobacter levanicum, transfructosylation reactions by levansucrase from, 91
Alcohol, the nitric acid oxidation of *iso*-amyl, 70
Alkaline earth nitrates in nitric acid solutions, 252
Alkylation of sodium salts of dialkyl phosphites, 83
o-alkyl-methylphosphonyl chlorides, synthesis of, 84
Amino alkyl sulphonic acids, antimetabolic activity of, 46
α-amino-β-hydroxy acids by reaction of 2,3-epoxy-acids with benzylamine, 55
Aminolactone method, synthesis of peptides of homoserine and of α, γ-diaminobutyric acid by an, 59
Ammonia (liquid), isotopic exchange of hydrogen with, 220
Ammonia reaction (chloramine), in water, 221
Ammonium perchlorate, thermal decomposition of, 206
Analog computer in the chemical industry, 234
Anion exchangers, distribution of zinc chloride between, 246
Anisole (*o*-iodo), the deiodination reaction of, 69
Antibodies, isolation of, from antigen-antibody complex, 112
Antigen
  —antibody complex, isolation of antibodies from, 112
  (a specific), a synthetic polypeptide with properties of, 111
  selective proteolysis of, 112
Antigenic surface compound. isolation of, 113
Antimetabolic activity of amino alkyl sulphonic acids, 46
Approximate treatment of the kinetics of parallel reversible reactions, 217
Aqueous hydrochloric acid-uranyl chloride-tri n-butyl phosphate, 248
Arginase, a *p*H-static method for the assay of, 105, 149
Aromatic hydrocarbons, reaction of diethyl oxalfluoroacetate with, 193
Aromatic ketones, paper chromatography of 2,4-dinitropnenylhydrazones of, 43
ATP formation in photophosporylation, 99

B

Benzene, adsorbed, spectrum of, 217
6,7-benzocoumaran-2-ones, a novel synthesis of, 81
Benzoyl-(polyalanine)-anilides, preparation and UV spectra of, 121
Benzoyl-(polyglycine)-anilides, preparation and UV spectra of, 121
Benzylamine, synthesis of α-amino-β-hydroxy acids by reaction of 2,3-epoxy-acids with, 55
Bicarbonate buffer solutions, 256
Biosynthesis of the sphingolipids, 87
  lipids in insects, 88
Bis-trialkylammoniumalkanol esters of carbonic acid, 108
Bleaching of pulp from Corn stalks, 241
Book reviews: —
  "Heterocyclic Chemistry, an introduction, "by A. Albert, 209
  "Chromatographic Reviews, Progress in Chromatography, Electrophoresis and Related Methods, "Vol. I, ed. by M. Lederer, 209
  "The Enzymes. Vol. I: Kinetics, Thermodynamics, Mechanism, Basic Properties", ed. Boyer, Lardy, Myrbaeck 210
ω-bromocarboxylic acid esters, preparation of linera, 68
Bromo-lactones, iodo-lactones and, 78
Bromination of indoles in aqueous and nonaqueous media, 61
Bromine (in TBE), reaction of acetylene with solutions of, 70
Bromoacetate
  and hydroxyl ions, 195
  (ethyl), telomerization of ethylene with, 68

C

Carbamoyl-phosphate, hydrolysis of, 225
Carbobenzoxyamino acid amides with carbonyl compounds, 55
Carbonate, titration of, 256
Carbonyl compoumds, reactions of carbobenzoxyamino acid amides, 55
Carcinogenic series, fluorine-containing polycyclic compounds of, 85
Catalysis (chloride ion) of the isotopic exchange between nitrate ions and water, 224
  of the mutarotation of poly-L-proline, 118
Caustification of potassium and sodium chlorides with calcium hydroxide, 238
Cellbound penicillinase and exopenicillinase in the γ-state, 28
Cellulose
  fibre formation, 116
  synthesis of, 94
C-esterase, purification of 106
Chemical
  composition of pollen from *Pinus canariensis*, 157
  Society, Proceedings of XXVIth Meeting of the Israel, 5
Chicks' intestines, proteolytic activity of, 23
Chloral, reaction with dialkyl thiophosphites, 82
Chloramine ammonia reaction in water, 221
Chloride
  complexes by anion exchange, 254
  ion catalysis of the isotopic exchange between nitrate ions and water. 224
  ions on the nitrate determination by Leithe's method, 255
  (uranyl), 223
Chlorides, metal, thermal hydrolysis of, 161
Chlorine, the mechanism of the hydrolysis of, 222
Chloroethanol — water mixture, helix-coil transition of poly-1-glutamic acid in, 138
Cholinesterases. hydrolytic activity of, 5
Choline esters. biological effectiveness of, 5
Chromatography (paper) of 2,4-dinitrophenylhydrazones of aromatic ketones. 43
Chromium trioxide — pyridine oxidation of substituted 1-3-propanediols. 86
Chromophores. different cross-conjugated. 76
Citric acid cycle intermediates, 94
Cobaltous chloride and manganous chloride, 161
Computer (analog) in the chemical industry, 234
Concentration of phosphate rock, 237
Conformational analysis by means of dipole moments and spectra, 76
Conjugative transmissions in the vinycyclopropane systems, II, 77

Copper
  by line precipitation of, 238
  -pyrophosphate solutions, 247
  triphosphate solution, ion-exchange equilibria in, 37
Corn
  pith as a raw material for papermaking, 242
  stalks, pulp from, 240
  bleaching of pulp from, 241
Cross-conjugated chromophores, 76
Cucurbitacins, structure of, 72
Curare-like activity, a new series of compounds showing, 108
α-cyanocinnamic acids, preparation and decarboxylation of, 62
Cyclic
  addition of malcic anhydride to α-cyclopropylstyrene,77
  carbonates,Grignard reaction of, 69
α-cyclopropylstyrene, cyclic addition of malcic anhydride to 77
Cystathionine, syntheses of polymeric polypeptides of, 66
Cysteine (S-acetyk) monomeric derivatives and polymers of, 64

D

DC arc, influence of some volatile elements on the intensities of spectral lines of Sm, Eu, Gd, and Dy in, 173
Decarboxylation of α-cyanocinnamtc acids, 62
Deiodination reaction of *o*-iodo anisole, 69
Dephenylmethane, higher homologues of, 80
Determining vapour pressures, a new method of, 248
Dialkyl thiophytes, reaction with chloral, 82
-diaminobutyric acid
  derivatives, 56
  synthesis of, by an aminolactone method, 59
Diethyl oxalofluoracetate
  properties of, 85
  reaction with aromatic hydrocarbons, 193
Dimerization (electrochemical) of acrylonitrile to adiponitrile, 244
Dimethylformamide and tetrahydrofurane, 228
2,4-dinitrophenylhydrazones of aromatic ketones, paper chromotography of, 43
Dipole moments and spectra, conformational analysis by means of, 76
Disodium benzophenone, polymerisation of acrylonitrile, styrene and methyl methacrylate by, 185
Distillation columns
  multicomponent, 235
  packed, 235
Diterpenes, potential intermediates for the synthesis of, 204
2,2'-Dithio-diethyl sylphide as an analytical reagent for nickel, 255
D-lactic dehydrogenase from *Leuconostic mesenteroids*, 95
DL-lysine methyl ester, tryptic hydrolysis of, 101
DPPD in fowl's tissues, deposition of, assessed by new method, 110

E

Egg white, proteolytic activity in, 103
Electric field effect in polymerization and some of its consequences, On an, 230
Electrochemical dimerization of acrylonitrile to adiponitrile, 244
Electrolysis of hydrogen peroxide ($H_2O_2^{16,16}$) in highly enriched H_2O^{18}, 224
Electrolytes, effects of, on CB-γ-penicillinase, 31
Electromicroscopic studies of cellulose fibre formation, 116
Electromigration, pulse technique in isotope separation by,
Enterobacteriaceae, TPNH specific hydroxylamine reductase in, 98
Enzymatic
  oxdation of 6-mercaptopurine, 96
  hydrolic rates and biological potency, 11
  synthesis of α-glucosyl 2-deoxyglucose, 92
Enzyme
  from rat liver, 122
  systems in adipose tissue, 25
2,3-epoxy-acids, reaction of, with benzylamine, 55
Equilibrium studies in the system KCl-HCl-*n*BuOH-H_2O, 177
Erythrosytes, glucose-6-phosphate dehydrogenase, 115
Esterification, fatty acid
  enzyme systems in adipose tissue in, 15
  in adipose tissue, 88
    relation to fat mobilization 90
  in

Esters of carbonic acid, bis-trialkylammoniumalkanol, 108
Ethanol irradiated with X-rays, 218
Ethyl carbamate (urethan), influence of, on nucleic acid metabolism, 121
Ethylene
dibromide, production via solvent extraction, 243
    reaction of ethylene with dilute solutions of bromine in, 243
Evacuated water solutions of ethanol irradiated with X-rays, 218
Exopenicillinase in the γ-state, 28
Expansion of a solid due to the adsorption of non-polar gases, 231
Extraction of HCl with TBP and third phase formation, 249

F

Ferrites (garnet type) 251
Ferro-ferricyanide action of X-rays on aqueous solutions of, 219
Flash-excitation of acridine orange in solution, 215
Fluoborates, hydrolysts of 221
Fluoride compounds, (inorganic) production of, 240
Fluorine compounds, organic, 193
Fluorine-containing polycyclic compounds of the carcinogenic series, 85
Fluoro-analogs of mevalonic acid and related compounds, 71
Fluoropyruvate and glutathione, effect of particle-bound γ-grutamyltranspeptidase on, 105
Forage constituents (water soluble) and their influence on metabolic activity of rumen, 143
Free counter diffusion by a new light absorption method, 233

G

Galactose absorption in the small intestine, 91
Garnet-type ferrites containing praesodynium or lanthanium, 251
α-glucosyl 2-deoxyglucose, enzymatic synthesis of, 92
Glucose-6-phosphate
  conversion of β-glucose-1-phosphate to, 93
  dehydrogenase of erythrosytes 115
β-glucose-1-phosphate to glucose-6-phosphate, conversion of, 93
Glutamine synthetase and glutamotransferase 125
Glutamotransferase in sheep liver enzyme preparations, 125
γ-glutamyltranspeptidase, particle-bound, effect of, 105
Glutathione and fluoropyruvate, effect of particle-bound -glutamyltranspeptidase on, 105
Glycerol (release of) during mobilization of unesterified fatty acids, 90
Grignard reaction of cyclic carbonates, 69
Guanidine HCl, penicillinase in, 104
2-guanidoethyl thiosulphuric acid, 35

H

Halide ions in solution, oscillator strengths of absorption bands of, 216
HCl with TBP, extraction of, 249
Heavy liquid cyclone (TBE), separation of minerals by, 236
Helix-coil transition of poly-l-glutamic acid, 138
Heterogeneous equilibria in the system aqueous nitric acid, 249
Heteropoly blue method for silica determination, 254
Homogeneous polyacid-polybase fibers, 230
Homologues (higher) of diphenylmethane, 80
Homoserine (protected), synthesis of, 56
6-Hydrazinopurine towards mammalian xanthine oxidase, behavior of, 94
Hydrochloric acid, hydrolytic degradation of tri n-butyl, phosphate in the presence of ,223
Hydrodynamtc properttes of poly-ε-carbobenzoxy-L-lysine 116
Hydrogen
  bonds in polyserine, 119
  evolved from evacuated water solutions of ethanol, 218
  isotopic exchange of, with liquid ammonia, 220
  peroxide $H_2O_2^{16,16}$ in highly enriched H_2O^{18}, 220
Hydrolysis
  curves of cholinesterase enzymes 10
  of carbomoyl-phosphate, 225
  of chlorine, the mechanism of the, 222
  of fluoborates, 221
Hydrolitic

  activity of cholinesterases, 5
  degradation of tri n-butyl phosphate, 223
Hydroxyl ions, reaction between bromoacetate and, 195
Hypochlorite, oxidation of cotton by, 226

I

Indoles, bromination of, in aqueous and non aqueous media, 61
Influence of
  polyelectrolytes on absorption spectra of acridine orange, 215
  saturated hydrocarbons on the rate of polymerization of olefines, 229
  some volatile elements on the intensities of spectral lines of Sm, Eu, and Dy in the DC arc, 173
Inorganic fluoride compounds, production of, 240
Inositols, a stereospecific total synthesis of, 72
Intermolecular cyclization by polyphosphoric acid, 82
Intramolecular
  energy transfer, 215
  phase-transitions in polymethacrylate salts, 232
"Invasion" of an ion-exchange membrane, difference of, 246
Iodine sensitivity of CB-γ-penicillinase, 29
    of exopenicillinase in γ-state. 32
Iodo- and bromo-lactones, 78
Ion-exchange
  equilibria in triphosphate and copper triphosphate solutions, 37
  membrane by monovalent and polyvalent ions, 246
  study of pyrophosphate and copper-pyrophosphate solutions, 247
Ionic effects, specific, on reaction rates, 195
"Isopotential naphelometry", 232
Isotope
  effects, molecular and atomic, in radiation chemistry o water solutions, 219
  separation by electromigration. pulse technique in, 207
Isotopic exchange
  of oxygen, 223
  of hydrogen, 220
Israel
  Chemical Society, Proceedings of XXVIth Scientific Meeting, 55
  patents, a review of, 237

K

Kinetic aspects of mild oxydation of wheat starch, 227
Kinetics of parallel reversible reactions, approximate treatment of, 217
KCl-HCl-*n*BuOH-H_2O, equilibrium in the system, 177
$KClO_4$, $KClO_3$ and $KBrO_3$, pyrolytic decomposition of, 252

L

Lactones, iodo- and bromo-, 78
Lanthionine, synthesis of polymeric polypeptides of, 65
Leithe's method, influence of chloride ions on the nitrate determination by, 255
Levansucrase, transfructosylation reactions by, 99
Lipids (in insects), biosynthesis of, 88
Liver
  (rat), enzyme from, 122
    mitochondria, spontaneous swelling of, 99
  (sheep), enzyme preparations, 125
Lysine and methionine, levels of, in portal blood of rats, 111

M

Magnesium oxide, thermal decomposition of ammonium perchlorate in the presence of, 206
Malcic anhydride, cyclic addition of, to α-cyclopropylstyrene, 77
Mammalian xanthine oxidase (XO), 94
Manganous chloride, cobaltous chloride and, 161
Mechanism of the hydrolysis of chlorine, 222
Meeting (XXVIth Scientific) of the Israel Chemical Society, 55
β-mercaptoethylamines derivatives of. as protecting agents against radiation, 107
6-mercaptopurine, enzymatic oxidation of, 96
Metabolic activity of the rumen, 143
Metacyclophane (5:5), preparation of, 82
Metal chlorides. thermal hydrolysis of, 161
Metal ketyls as initiators of polymerisation of vinyl monomers, 185
Methionine and lysine, levels of, in portal blood of rats, 111
3-methylpurines, synthesis and properties of, 74
Mevalonic acid, fluoro-analogs of, 71
Micrococcus pyogenes (var. aureus), resistance of, to basic polypeptides, 109
Mitochondria (rat liver), spontaneous swelling of, 99
    (Novikoff tumor), enzymatic activity of, 100
Model reactions and attempted synthesis of a potential pentalene system, 80
Molar polarizations in the adsorbed states, 231
Molecular and atomic isotope effects in radiation chemistry of water solutions, 219
Mono-fluoromalonate, toxicity and biochemical effects of, 109
Monomeric derivatives and polymers of S-acetyl cysteine, 64
Monovalent and polyvalent ions, "invasion" of an ion-exchange membrane by, 246
Multicomponent distillation columns, 235
Mutarotation of poly-1-proline, changes accompanying, 130
Myosin, nucleoide triphosphatase activity of, 100

N

N-acylphosphoramidic acids, solvolysis of, 226
N-benzyl-DL-aspartic acid, resolution of, 49
Nickel, 2,2"-Dithio-diethyl sylphide as an analytical reagent for, 255
Nitrate ions and water, chloride ion catalysis of the isotopic exchange between, 224
Nitric acid
  isotopic exchange of oxygen between hydrogen peroxide and water catalysed by, 223
  oxidation of iso-amyl alcohol, 70
Nitroethylene, polymerization of, 228
Non-polar gases, adsorption of, 231
Novikoff tumor enzymatic activity of, mitochondria,
N-oxides, (organic), as complexants, 245
Nucleic acid metabolism, influence of ethyl carbamate (urethan) on, 121
Nucleotide triphosphatase activity of myosin, 100

O

o-iodo anisole, the deiodination reaction of, 69
Oleuropein, the bitter principle of olives, 92
Olefines, polymerization of, 229
Olives, oleuropein, the bitter principle of, 92
Optical rotatory dispersion and viscosity changes accompanying mutarotation of poly-1-proline, 130
Organic
  Chemistry (Section of) and Biochemistry, Israel Chemical Society, 55
  organic N-oxides as complexants, 245
Oscillator strengths of the absorption bands of halide ions in solution, 216
Oumnova acyloin rearrangement, 68
Oxydation of
  cotton by hypochlorite, 226
  iso-amyl alcohol, 70
  6-mercaptopurine, 96
  2-aminopurines by mammalian xanthine oxidase, 97
  wheat starch by sodium hypochlorite, 227
Oxygen, isotopic exchange of, 223

P

Packed distillation columns, 235
Paper chromatography of 2,4-dinitrophenylhydrazones of aromatic ketones, 43
Papermaking, corn pith as a raw material for 242
Parallel reversible reactions, approximate treatment of kinetics of, 217
Pasteurella pestis, 113
Penicillinase
  cellbound, 28
  in guanidine HCl, 104
Pentalene (potential) system model reactions and attempted synthesis of a, 80
Pepsin, conversion of, to pepsin, 102
Pepsinogen, conversion of, to pepsin, 102
Peptides (synthesis of) of homoserine and of α,γ-diaminobutiric, 59
Perm-selective membranes, 114
Phenol, for increasing the solubility of potassium and sodium chlorides, 238
Phenyl lythium, syntheses with, 79

Phosphate rock, concentration of, 237
Phosphorus pentoxide with alcohols reaction of, 254
Phosphorylation product of poly-DL-serine, 63
Photochemical decomposition of TBE 70
Photoelectric scanning, 233
Photophosphorylation by chloroplasts, 99
*p*H-static method for the assay of arginase, 105, 149
Physiological membrane phenomena, possible model for, 114
Pinus canariensis, pollen from, 157
Poisoning and sign reversa, of perm-selective membranes, 114
Polarizations (molar) in the adsorbed state, 231
Pollen from *Pinus canariensis*, 157
Polyacid-polybase fibers, homogeneous, 230
Polyamino acids, (multichain), synthesis and properties of some, 117
Polycyclic compounds of the carcinogenic series, containing fluorine, 85
Poly-DL-homocysteins preparation and properties, 65
Poly-DL-serinet a phosphorylation product of, 63
Poly-ε-carbobenzoxy-L-lysine, hydrodynamic properties of, 116
Polyelectrolytes, influence of, on absorption spectra of acridine orange, 215
Polyethylene as a constructional material, 237
Poly-l-glutamic acid, helix-coil transition of 138
Poly-L-proline
  catalysis of the mutarotation of, 118
  in solution mutarotation of. 130
Polymeric polypeptides of lanthionine, 65
  cystathionine 66
Polymerization
  an electric field effect in, 230
  of acrylonitile styrene and methyl methacrylate, 185
  of olefines, 229
  of nitroethylene in dimethylformamide and tetrahydrofurane 228
  of vinyl monomers, metal ketals as initiators of, 185
Polymers of S-acetyl cysteine, 64
Polymethacrylate salts, phase transitions in, 232
Polypeptide, a synthetic, with properties of a specific antigent, 111
Polypeptides
  (basic), resistance of *Micrococcus pyogenes* (var. aureus), 109
  (polymeric) of cystathionine, 66
    lanthionine, 65,
Polyphosphoric acid, intermolecular cyclization by, 82
Polyserine, hydrogen bonds in, 119
Potassium
  chloride and sulphuric acid, 239
  and sodium chlorides, caustification of, 238
  perrhenate, 249
  sulphate from potassium chloride and sulphuric acid, 239
Praesodymium or lanthanium in garnet-type ferrites, 251
Precipitation of copper by lime as an alternative to cementation, 238
Proceedings of the Israel Chemical Society, 215
1,3-propanediols — (substituted) chromium trioxide-puridine oxidation of, 86
Properties of the sulphur-oxygen bond, 226
Proteolysis (selective) of the antigen, 112
Proteolytic activity
  in egg white 103
  of chicks' intestines, 23
  measurement of, 25
Proceedings of the XXVIth Scientific Meeting of the Israel Chemical Society, 55
Pulp from corn stalks 240
Pulse technique in the isotope separation by electromigration, 207
Pyrolytic decomposition of $KCLO_4$, $KClO_3$, $KBrO_3$ 252
Pyrophosphate and copper pyrophosphate solutions, 247

R

Radiation
  chemistry of water solutions, 219
  derivatives of β-mercaptoethylamines, 107
Radioisotopes in the titration of halogens, use of, 253
Reaction rates, specific ionic effects on, 195
Ribonucleic acid, ribonucleotide incorporation into, 122
Ribonucleoproteins, biochemical differences in 123
  antibodies in, 123
Ribonucleotide incorporation into ribonucleic acid, 122
Ring enlargement reactions, 78
Rumen, metabolic activity of, 143
Ruthenium tetroxide in nitric acid solutions, 250

S^{35}, use of, in syntheses and exchange reactions, 87
S-acetyl cystein, monomeric derivatives and polymers of, 64
Saturation effect in the system aqueous hydrochlorte acid-uranyl chloride-tri n butyl phosphate, 248
Separation of
  metals as chloride complexes by anion exchange, 254
  minerals by heavy liquid (TBE) cyclone, 236
Serine-phosphate, solvolysis of, 228
Shift and optical rotation of penicillinase in guanidine HCl, 104
Silica determination, the heteropoly blue method for, 254
Society, Scientific, Proceedings of the XXVIth Meeting of Israel Chemical. 55
Sodium
  chlorides and potassium, caustification of, 238
  salts of dialkyl phosphites, alkylization of, 23
Solubility of mixed crystals of alkaline earth nitrates in nitric acid solutions, 252
Soluble (in water) forage constituents and their influence on metabolic activity of rumen, 143
Solvolysis of
  N-acylphosphoramidic acids, 226
  serine-phosphate and related compounds, 228
Solvent extraction, ethylene dibromite production via, 243
Solute-water-organic solvent systems, 248
Specific ionic effects on reaction rates: the reaction between bromoacetate and hydroxyl ions, 195
Spectra, conformational analysis by means of, 76
Spectral lines of Sm, Eu, Gd and Dy in the DC arc, influence of some volatile elements on the intensities of, 173
Spectrum of adsorbed benzene, 217
Sphingolipids, biosynthesis of, 87
γ-state, exopenicillinase in, 28
Stereospecific total synthesis of inositols, 72
Stromatic factor used in activation of glucose-6-phospate dehydrogenase of erythrosytes, 115
Sulphonic acids (amino alkyl), antimetabolic activity of, 46
Sulphur-oxygen bond, properties of, 226
Synthesis of
  cellulose by *A. xylinum* cells, 94
  diterpenes, 204
  dl- and d--podocarpan-6-one 204
Sylphide (2,2''-Dithio-diethyl) as an analytic reagent for nickel, 255
System KCl-HCl-*n*BuOH-H_2O, equilibrium studies in the, 177

T

(TBE) cyclone, separation of minerals by heavy liquid, 236
TBP, extraction of HCl with, 249
Telomerization of ethylene with ethyl bromoacetate, 68
Tetrabromoethane
  photochemical decomposition of, 70
  reaction of acetylene with solution of bromine in, 70
  (TBE), polethylene as a constructional material for use with, 237
Tetroxide, (ruthenium) in nitric acid solutions, 250
Thermal
  decomposition of ammonium perchlorate, 206
  hydrolysis of metal chlorides, II, 161
6-Thiouric acid and some of its derivatives, 73
Thiosulphuric acid, 2-guanidoethyl, 35
Titration of
  carbonate, 256
  halogens, 253
Toxicity and biochemical effects of mono-fluoromalonate, 109
TPNH specific hydroxylamine reductase in enterobacteriaceae, 98
Tracer experiments on the pyrolytic decomposition of, $KClO_4$, $KClO_3$ and $KBrO_3$, 252
Transfructosylation reactions by levansucrase, 91
Tri n-butyl phosphate, hydrolytic degradation of, 223
Triphosphate ions from triphosphate solutions, 38
Trypsin column, 101
Tryptic hydrolysis of DL-lysine methyl ester, 101

U

UFA, (unesterified fatty acids) from adipose tissue, 90

V

Vapour pressures, a new method of determining, 248
Vinycyclopropane systems, conjugative transmissions in, 77
Viscosity changes accompanying mutarotation of poly-l-proline, 130
Volatile elements, influence of some, on the intensities of spectral lines of Sm. Eu. Gd and Dy in the DC arc, 173

W

Water content and water partial vapour pressures, relationship between, 248
Wheat starch, some kinetic aspects of mild oxydation of, 227

X

$X=O^{18}$ groups stretching bands, absorption intensity of, 216
X-rays (action of) on aqueous solutions of ferro-ferricyanide, 219

Z

Zinc chloride between anion exchangers, distribution of, 246

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